TURBULENT DIFFUSION AND CHEMICAL REACTION IN A TUBULAR REACTOR

A THESIS

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Olin Maynard Fuller, Jr.

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Approved:

H. C. Lewis, Thesis Advisor

Wm. F. Atchison

H. C. Ward

Date Approved by Chairman January 16, 1962

ERRATA

Page	Location	Correction
87	Equation 86	$u^* = \sqrt{\frac{\tau_w g_c}{\rho}} = \bar{u}\sqrt{\frac{f_F}{2}}$
		$y' = \frac{y}{r_w} = \frac{r_w - r}{r_w}$
		$s = \frac{r}{r_w} = 1 - \frac{y^+}{Y^+} = 1 - y'$
88	Equation 88b	$\frac{du^+}{dy^+} = \frac{2s}{1 + \left[1 + 4s\left(\frac{Y^+ l_p}{r_w}\right)^2\right]^{1/2}}$
	Equation 89	$u^+ = \int_0^{y^+} \frac{2\left(1 - \frac{y^+}{Y^+}\right)}{1 + \left[1 + 4\left(\frac{Y^+ l_p}{r_w}\right)^2\left(1 - \frac{y^+}{Y^+}\right)\right]^{1/2}} dy^+$
	Line 11	From 83, 86, and 88b.
101	Equation 106b	Last term on left side should read: $Q_2 R(\gamma, \theta)$
102	Equation 106d	$\widehat{D}(s) = \frac{1}{D^*}\left\{D_m + \frac{\alpha_m \nu}{2}\left[(1 + 4\phi^2)^{1/2} - 1\right]\right\}$
	Equation 107d	Replace τ by θ.
	Line 10	Second factor on right side should read: $\left(\frac{\nu_2}{\nu_1}\right)^m$

Finally, the author is grateful for the encouragement, loving understanding, and timely help given him by both his wife and his parents.

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SUMMARY

The study reported in this thesis had as its objective the development of an improved method for predicting the behavior of homogeneous chemical reactions in tubular reactors. The study is divided into a theoretical phase and an experimental phase. The purposes of the theoretical investigation were, first, the formulation of a mathematical model that would fulfill the overall objective and, second, the development of a method of calculation that would permit numerical results to be obtained from the mathematical model. The purposes of the experimental investigation were, first, to provide data for comparison with theoretical results and, second, to test some of the assumptions on which the theoretical formulation was based.

The published studies most closely related to this one are those of Chambré (100) and Cleland and Wilhelm (98). Chambré considers homogeneous reactions in tubular reactors. He permits heat exchange between the reaction mixture and the vessel wall, heat generation or absorption by the reaction, and an arbitrary velocity distribution. However, the physical properties of the reaction mixture, including the radial diffusivities of heat and mass, are assumed to be constants. The mathematical model of Chambré constitutes a boundary value problem which includes two non-linear, partial differential equations. These equations are transformed by a substitution of "the generalized isothermal reaction time," and the resulting equations are linearized by developing the new

variable in a perturbation series. The linearized version of Chambré's boundary value problem is solved by the separation of variables and the application of Sturm-Liouville methods to the resulting systems. It is noted that the approximation used to linearize the partial differential equations in Chambré's problem is poor for liquid-phase reactions and laminar flow because of the smallness of the molecular diffusivity of mass. No numerical results or experimental measurements are included in this study.

Cleland and Wilhelm studied the behavior of first-order, isothermal, homogeneous reactions in tubular reactors. They considered only a parabolic velocity distribution and constant physical properties. The mathematical model used by Cleland and Wilhelm contains only one partial differential equation and its associated boundary conditions. They obtained analytical solutions for two limiting cases of this boundary value problem. For the general case, they used the numerical method of Crank and Nicolson (99) to compute particular, approximate solutions. Cleland and Wilhelm also conducted an experimental investigation employing the aqueous hydrolysis of acetic anhydride, a pseudo-first-order reaction. Only bulk concentrations were measured, so information on radial concentration distributions cannot be obtained from these data. The computed and measured values of bulk concentration agreed quite well.

In the theoretical investigation of the present study, a mathematical model was developed to describe the steady state of a chemically reacting fluid passing through a tubular reactor. In this formulation

the character of the flow is turbulent, the physical properties of the fluid are constant, and heat transfer between the tube wall and the reaction mixture is permitted. The effects of the radial distributions of velocity and radially-directed diffusivities are emphasized. For this reason, the model is termed a "radial-diffusion" model. The use of this type of model made possible the calculation of radial concentration and temperature distributions as well as the bulk values of these variables.

The velocity and diffusivity distributions used in the mathematical model were found to play an important role in the computation of temperature and concentration distributions. For this reason, a critical examination of published velocity and diffusivity distributions was required. As the first step in this examination, the difficulty of extracting precise estimates of eddy diffusivity of momentum from currently available velocity data was demonstrated by a statistical analysis. This difficulty made it desirable to calculate eddy diffusivity distributions from the velocity distributions and caused the accuracy of the chosen velocity correlation to be even more important. The second step in the examination was the statement of seven criteria of merit for velocity correlations. Finally, eight typical velocity correlations were judged according to these seven criteria. None of the eight correlations satisfied all seven criteria for values of Reynolds number less than 40,000 and only one satisfied them for values greater than 40,000. The values of Reynolds number for the tests in the experimental investigation were all less than 12,000, for practical reasons, so that the comparison of

experimental and theoretical results required accurate velocity distributions for this range of Reynolds number. Thus, the search for a satisfactory velocity correlation became a necessary adjunct to the original problem of this study.

A new velocity correlation was developed which satisfies six of the seven criteria for values of Reynolds number from 3,000 to 50,000. According to the remaining criterion, that is, lack of conflict with experimental velocity data, the proposed correlation was judged to be good at Reynolds numbers of 5,000, 10,000, and 19,500 and fair at a Reynolds number of 39,500. The distributions of eddy diffusivity of momentum were obtained from this velocity correlation and the eddy diffusivities of heat and mass were related to the eddy diffusivity of momentum by an empirical equation.

For the calculations described in this thesis, the mathematical model was made somewhat less general by specifying the forms of the reaction rate expression and the boundary condition for heat transfer at the reactor wall. Some of the calculations constitute simulations of experimental heat transfer and chemical reaction tests. The remaining calculations illustrate parametric sensitivity, thermal initiation of chemical reactions, and programmed temperature control.

The mathematical model used for the calculations described here constitutes a boundary value problem in mathematics. This original boundary value problem was approximated first by substituting a system of non-linear, ordinary differential equations for the two non-linear, partial differential equations of the original problem. This system of ordinary differential equations was integrated numerically by means

of the backward difference approximation for a first derivative. The result was an approximate boundary value problem in which the derivatives of the partial differential equations and boundary conditions in the original problem were replaced by finite difference quotients. The nonlinear difference equations of this approximate boundary value problem were solved by an iterative method.

The mathematical literature was searched for theorems that would guarantee the validity of the numerical method used in this investigation. However, no applicable theorems were found, so that the validity of the method of numerical analysis as well as the validity of the mathematical model itself could be supported only by an agreement between experimental and computed results.

In the experimental investigation, velocity, temperature, and concentration distributions were obtained in a jacketed tubular reactor, one inch in diameter and fifteen feet tall. The reaction used in this experimental work was the aqueous saponification of methyl acetate by sodium hydroxide. The ranges of the operating variables covered in the experimental tests were Reynolds numbers from 4,500 to 10,000, initial concentrations from zero to one mole per liter, and jacket temperatures from zero to 40°C in excess of the inlet temperatures.

Several kinds of tests were carried out. In the isothermal flow tests, velocity and friction factor data were obtained. In the tests with flow and heat transfer, temperature and velocity profiles were determined. Chemical reaction tests were carried out both with and without hot water circulating through the reactor jackets. Concentration and

temperature distributions were obtained in these tests. Velocity data were also obtained for the latter condition.

The differences between the present study and the work of Chambré (100) and Cleland and Wilhelm (98) are worth mentioning. The main differences between this work and that of Chambré are the inclusion of distributed radial diffusivities in the mathematical model of the present study, the inclusion of numerical and experimental results, and the use of different methods of obtaining approximate solutions. This study differs from that of Cleland and Wilhelm by employing turbulent rather than laminar flow and by considering non-first-order reactions and the presence of heat transfer and an appreciable heat of reaction as well as first-order, isothermal reactions. The main difference between the experimental investigation of this study and the one of Cleland and Wilhelm is that the measurements show the radial distributions of concentration and temperature instead of the bulk values of these variables.

The experimental velocity data obtained in the present study show that the flow had the expected turbulent velocity distribution for isothermal conditions. Experimental values of the Fanning friction factor are slightly larger than those accepted for smooth pipe.

Temperature distributions were computed for two of the heat transfer tests of this study and two tests of Sleicher. The shapes of the computed distributions are in good agreement with the experimental data of these tests.

The chemical reaction tests conducted without the circulation of hot water in the reactor jackets showed little radial variation in

temperature and concentration throughout most of a reactor cross section. Therefore it is not surprising that the mathematical model of this study has no advantage over the simpler, piston-flow model for these conditions. On the other hand, the validity of the mathematical model of this study is supported by a three-way comparison of experimental data and outlet concentrations computed using the equations of a piston-flow model and the radial-diffusion model of this study.

Comparisons of experimental data with the velocity and temperature distributions computed for the tests combining chemical reaction with heat transfer show agreement within the precision of the experimental measurements.

The relatively simple method of numerical analysis used in the theoretical investigation of this study gave surprisingly good results. However, the need for adjustment of the value of (Δz) during computation and the slight disagreement with the results computed by the equation of a piston-flow model for one of the pseudo-adiabatic reaction tests indicate that further work is needed on the method of numerical analysis.

The illustrative calculations showed that the radial-diffusion model of this study is subject to parametric sensitivity in certain regions. The model yields different conditions for approximate chemical similarity than do axial-diffusion models. The assumptions of earlier methods of calculation for endothermic reactions in tubular reactors with preheat sections were shown to be questionable.

The objective of this study was largely, but not fully, obtained. The radial-diffusion model and method of numerical analysis

presented here are believed to need further development before they will be satisfactory for routine design calculations. However, the results of this combination of mathematical model and numerical method are believed to be sufficiently valid to justify the use of the combination in its present state as a research tool.

NOMENCLATURE

Because of the large number of physical quantities mentioned in this thesis, it has been necessary to define a few symbols in a way that is contrary to established convention. An example is the use of Z for heat capacity rather than the usual C_p. In addition, the attention of the reader is directed to the multiple use of the symbol υ. This symbol with a subscript is always a stoichiometric coefficient. If υ appears as an algebraic quantity, not a matrix, and has no subscript, it represents shear stress. It must be pointed out that symbols for variables and constants appearing in the purely mathematical writing at the end of Chapter II and in Appendix I are arbitrary and have no physical significance.

Numbers in parenthesis indicate equations where the symbol in question appears. When only one number is shown, this refers to the first equation where the symbol appears.

Units in brackets indicate the units that have been used consistently throughout the present study. These units will not necessarily apply to the material in Chapter II concerning previous contributions.

Subscripts

w	Indicates the evaluation of a quantity at the tube wall (6).
J	Refers to fluid in the reactor jacket
f	Refers to Reactor feed

Superscript

o	Refers to inlet condition
-	Refers to bulk values defined by equation 117

Symbol

$[A]$	Matrix defined after equation 111
A_H	Empirical constant, (25b)
A_R	Constant in reaction rate expression three paragraphs below equation 58
A_t	Cross-sectional area of reactor tube, (37)
$A_x = \frac{h_{Tx} r_w}{k_{Tw}}$	"External Nusselt number," (80)
a_{ij}	Elements of the matrix [A], (109, 111)
$[B]$	Matrix defined after equation 114
B	Constant in $k'_R = e^{B - E/RT}$, (105a)
b_{ij}	Elements of the matrix [A], (109, 111)
B_n	Parameter defined by Chambré , (46)
$[C]$	Matrix defined after equation 115
C	Concentration, [moles/ liter]
c	Concentration, [moles/ gram]
ϵ	Mass fraction, (54)
c_i^o	Inlet (or initial) concentration of i^{th} reactant, (73), [moles/ gram]
C_s	Measured sample concentration, (119), [moles/liter]
c_m	Variable defined by Chambré (49)
D	Diffusivity of mass $[(cm)^2/sec.]$

$D(s)$	Diffusivity of mass when it is considered a function of relative radius, $[(cm)^2/sec.]$
D_m	Molecular diffusivity, (18), $[(cm)^2/sec.]$
D_T	Taylor's virtual axial diffusivity, (20)
D^*	A value of $D(s)$ that is characteristic of the fluid properties and the nature of the flow. For this study, D^* = least upper bound of $D(s)$, $[(cm.)^2/sec.]$
$\hat{D}(s)$	$D(s)/ D^*$
d	Diameter, (28)
E	Activation energy, $[cal./mole]$
e	Combined emissivities of radiating and absorbing surfaces, (32)
$f(T)$	Temperature dependent part of rate coefficient, (51)
$f_c(s)$	Relative velocity used by Chambré, (46)
f_F	Fanning friction factor, (13b, 85)
g	Acceleration due to gravity, (118) $[cm./(sec.)^2]$
g_c	Gravitational constant, (5), $[(gm.)\ (cm.)/(gm.)_F(sec.)^2]$
$g(T)$	Temperature dependent part of rate coefficient (51)
$H(T)$	Functional defined by Bilous and Amundson, (52)
H_R	Heat of reaction, (26), $[cal./equivalent]$
h_M	Manometer reading, (118), $[cm.]$
$h(s,\xi)$	Specific enthalpy, weight basis, (55)
h_T	Heat transfer coefficient
h_{Tx}	External heat transfer coefficient, (80), $[cal./(cm.)^2(sec.)\ (^oC)]$

J	Total heat loss through the tube wall per unit time, (34)
$J(T)$	Functional defined by Bilous and Amundson, (52)
$J(\epsilon_j, T)$	Reaction rate as expressed by Chambré, (55)
K	Thermal diffusivity $[(\text{cm.})^2/\text{sec.}]$
$K(s)$	Thermal diffusivity when it is considered a function of relative radius, $[(\text{cm.})^2/\text{sec.}]$
K_m	Molecular thermal diffusivity, $[(\text{cm.})^2/\text{sec.}]$
K^*	A value of $K(s)$ that is characteristic of the fluid properties and nature of flow. For this study, K^* = least upper bound of $K(s)$, $[(\text{cm.})^2/\text{sec.}]$
$\hat{K}(s)$	$K(s)/K^*$
K_v	von Kármán's constant, Ref. 42
k_R	Ae^{-E/R_gT}, Reaction rate coefficient. The units of A depend on the form of the concentration dependent part of the reaction rate expression.
k'_R	$\exp(B-E/R_gT)$, Numerical part of reaction rate coefficient. This form was used for computer work to avoid handling excessively large or excessively small numbers.
k_T	Thermal conductivity, $[\text{cal.}/(^\circ\text{C})(\text{sec.})(\text{cm.})^2]$
L	Tube length, [cm.]
L	Operator used by Chambré, (55)
ℓ	A linear dimension that is characteristic of a piece of apparatus.
ℓ_P	Prandtl's mixing length parameter (12a), (12b) [cm.]
ℓ_j^*	An axial displacement that is characteristic of the j^{th} product, (42)

M — Molecular weight, (1)

N_H — Empirical constant used by Hawthorne, (25b)

$N_{Re} = \frac{2r_w \bar{u}}{\upsilon}$ — Reynolds number

$N_{Pr} = \frac{Z\mu}{k_T}$ — Prandtl number

$N_{Sc} = \frac{\mu}{\rho D_m}$ — Schmidt number, (32)

$N_{Nu} = \frac{h_T d}{k_T}$ — Nusselt number, (29)

$N_{DI} = \frac{U' \ell}{\mu}$

$N_{DII} = \frac{U' \ell^2}{D_m}$ — Damkoehler numbers, (26)

$N_{DIII} = \frac{H_R U \ell}{Z \rho \theta_D u}$

$N_{DIV} = \frac{H_R U \ell^2}{k_T \theta_D}$ — Damkoehler numbers, (26)

n_D — Empirical constant, (25a)

$P_1 = \frac{LK^*}{\bar{u} r_w^2}$, (106a)

$P_2 = \frac{LD^*}{\bar{u} r_w^2}$, (106b)

P — Pressure, $[(gm.)_F/(cm.)^2]$

$P_i = \frac{\rho \bar{u}^2}{2g_c}$, Impact pressure, (123) $[(gm.)_F/(cm.)^2]$

P_G — Parameter of Gill and Scher, (14)

$(\overrightarrow{P/u})$ Vector defined after equation 111

p_1, p_2 Parameters, (92)

$p_c = \lambda_c/(1 - s^2)$, Parameter used by Cleland, (45)

$$Q_1 = \frac{R_g L H_R U^*}{E \bar{u} Z \rho}, \quad (106a)$$

$$Q_2 = \frac{L U^* v_i}{\rho \bar{u} c_i^2}, \quad (106b)$$

$(\overrightarrow{Q/u})$ Vector defined after equation 111

Q_w Heat flux density at the tube wall, (33), [cal./(sec.)(cm.)^2]

$\vec{q}$ Vector defined after equation 111

q_w Heat flux at the tube wall, (57), [cal./sec.]

$\vec{R}$ Vector defined after equation 111

$R(\gamma,\theta) = U/U^*$, Dimensionless reaction rate

R_g Ideal gas law constant, [cal./(mole)(°C)]

r Radial displacement from the axis of a tube, (6), [cm.]

r_c Radial displacement defined in equation 123, [cm.]

S Internal diameter of an impact-pressure probe, (122) [cm.]

S_e External diameter of an impact-pressure probe, (122), [cm.]

$s = r/r_w$, Relative radius, (6)

T Temperature, [°K unless specified otherwise]

T_r Absolute temperature of corresponding points on radiating surfaces, (32)

t Time, [sec.]

t_s Mean residence time in sampling line, (119), [sec.]

t_R Mean residence time in reactor tube, (129, 130), [sec.]

U Reaction rate, (26), [equivalents/(liter)(sec.)] The dimension, "equivalent," used here is a gram molecular weight of a component of some reaction mixture, divided by the stoichiometric coefficient for this component.

$U' = \frac{\upsilon_j U}{C_j^o}$, Reaction time constant for j^{th} reactant, [$(sec.)^{-1}$]

U^* Unit reaction rate, [equivalents/(liter)(sec.)]

u Temporal-mean velocity [cm./sec.] Characteristic velocity, (26, 30), [cm./sec.]

$u(s)$ Temporal-mean velocity when it is considered a function of relative radius, (5), [cm./sec.]

$\bar{u}$ Bulk velocity, (7), [cm./sec.]

$\hat{u}(s) = u(s)/\bar{u}$, Relative velocity, (86)

$u^* = u(s)/\bar{u}$, Relative velocity (86)

$u^+ = u(s)/(\tau_w g_c/\rho)^{\frac{1}{2}} = u(s)/u^*$, (6, 86)

$u^{++} = u^+ (\bar{u}/u_{max})$

u_{max} = Maximum value of $u(s)$, [cm./sec.]

$\vec{V}$ Vector defined after equation 111

V_s Volume of sampling line, (120), [$(cm.)^3$]

v Volumetric flow rate, (34)

v_s Volumetric flow rate of sampling stream, (120), [$(cm.)^3/sec.$]

W Conversion per pass or per batch, (3)

$W(t)$ Batch conversion as a function of time, (37)

w_n Variable defined by Chambré, (47)

X Scaling factor

x Axial displacement from reactor inlet [cm.]

Y Yield, (4)

$y^+ = r_w u^*/\upsilon$, (86)

y Displacement from the tube wall along a radius, (5) [cm.]

$y' = y/r_w$, (86)

$y^+ = (y/r_w)(r_w/\upsilon)(\tau_w g_c/\rho)^{\frac{1}{2}}$

$y^{++} = y^+ u_{max}/\bar{u}$

y_v Virtual displacement of a probe from the tube wall, (123), (125c), (126), (127) [cm.]

y_o Displacement of a probe center line from the tube wall, [cm.]

y_n Variable defined by Chambré (46)

Z Heat capacity at constant pressure, [cal./(gm.)(°C)]

$z = x/L$ Dimensionless length

$\alpha = \frac{k_R r_w}{D\rho}$, (49)

$\alpha_m = \varepsilon_m/\varepsilon_v$, (106d)

$\alpha_H = \varepsilon_H/\varepsilon_v$, (106e)

$\beta = r_w/D\rho$, (54)

β_D Deissler's heat flux parameter

γ = Fraction unconverted of a reference component, (31)

Γ Final value of γ, (39b)

δ_j^T Loss in selectivity for j^{th} product due to axial mixing, (42)

$\delta_v = y_v - y_o$, Difference between the virtual displacement of a probe and the displacement of the probe center line, (122)

δ_n Constant defined by Chambré, (46)

δ_s Stoichiometric constant, (3-39a)

Δ Finite difference operator $\Delta W_n = W_{n+1} - W_n$

∇ Finite difference operator $\nabla W_n = W_n - W_{n-1}$

$\Delta_{si} = \frac{\upsilon_1 C_n^o - \upsilon_n C_1^o}{\upsilon_n C_1^o}$ Stoichiometric constant, (73)

ε_v Eddy diffusivity of momentum, (5) $[(cm.)^2/sec.]$

ε_m Eddy diffusivity of mass, $[(cm.)^2/sec.]$

ε_H Eddy diffusivity of heat, $[(cm.)^2/sec.]$

$\zeta = x/2D\bar{u} r_w$, (48)

η Displacement transverse to flow from an arbitrary fixed point, (122), [cm.]

$\theta = \frac{TR_g}{E}$ Dimensionless temperature

$\theta^o = \frac{T^o R_g}{E}$ Dimensionless inlet temperature

$\theta_J(z) = \frac{T_J(z) R_g}{E}$

θ_D Excess temperature (26)

$\theta_c = \frac{Z(T - T_w)}{H_R}$ (49)

Λ Pre-exponential factor of rate coefficient k_R

$\lambda_H = D_m/uL$ (31)

$\lambda_c = k_R x/u_{max}$ (45)

λ_n	Constant defined by Chambré (47)
μ	Viscosity [gm./(cm.)(sec.)]
υ	Kinematic viscosity [(cm.)^2/sec.]
υ_A, υ_i	Stoichiometric coefficients (1)
$[\upsilon]$	Matrix of stoichiometric coefficients (72b)
ξ	Extent of reaction, (70) [equivalents]
ξ_c	Extent of reaction defined by Chambré, Ref. 100, (48)
ρ	Density (5) [gm./(cm.)^3]
σ	Stefan-Boltzmann constant (32) Standard deviation (Appendix I)
τ	Shear stress, (5) [$(gm.)_F$/(cm.)^2]
τ_c	Generalized isothermal reaction time
φ	Function defined by equation 96
χ	Chemical efficiency, (2)
ψ	An unknown function (32)
$\omega_a, \omega_b, \omega_c$	Parameters, (101, 103)

CHAPTER I

INTRODUCTION

This research is concerned with a problem in the field of chemical reaction engineering, namely, the prediction of conversions of homogeneous reactions in continuous-flow, tubular reactors when the character of the flow is turbulent and the physical properties of the fluid are constant.

Before considering the work undertaken for this project, several important topics, which might otherwise be obscure to the reader, are discussed in the first part of this chapter. In the second part, the theoretical problems attacked in this project are introduced. Then, the objective of the study and the a priori limitations of the results are stated. Finally, the plan of the investigation is presented.

Topics in Chemical Reaction Engineering.--The principal aims of chemical reaction engineering are the prediction and control of chemical conversion on an industrial scale and the rational design of chemical reactors. The attainment of these aims should lead to the most economically favorable design and operation of industrial processes involving chemical transformations.

The first three topics discussed below concern complications encountered in dealing with chemical reactions on an industrial scale. These complications are interactions between phenomena, competing reactions, and programmed control. Finally, some general limitations

on the application of theories in chemical reaction engineering are mentioned.

The role of the interactions between chemical and physical phenomena is especially important in chemical reaction engineering. The situation is expressed well in the celebrated section of Der Chemie-Ingenieur written by G. Damkoehler in 1939 (1). The first paragraph is quoted below (translation by the writer):

> In most cases, the entire kinetic course of a chemical process is controlled not only by the true chemical reaction velocity, but also by diffusion and flow processes and the particular kind of thermal behavior.[1] Certainly, the general laws followed by these partial processes are almost completely known. Attention is called to the extensive fields of fluid dynamics and heat exchange. Although these partial fields have been investigated widely, a combination of them with typical chemical processes has hardly been handled up to now. Yet diligent work on this theme is especially desirable since the true chemical process seldom is separable in practice from the so-called pure physical processes.

This emphasis on the importance of the interactions between the various phenomena is echoed in the syllabus of the Symposium on Chemical Reaction Engineering (2) held in 1957 by the European Federation of Chemical Engineering. This syllabus states in part:

> An important part is played by various factors such as flow phenomena, mass and heat transfer, and reaction kinetics. It will be clear that in the first place it is necessary to know these factors separately.
>
> Yet this knowledge in itself is insufficient. The development of chemical conversions on a technical scale can only be understood from the relation and interaction between the above mentioned factors.

---

[1] The writer interprets ". . . the particular kind of thermal behavior, . . ." to include both the effect of heat released or absorbed due to the reaction and the effect of heat transfer between the reaction mixture and the surroundings.

Although the interactions between phenomena play a key role in most industrial chemical reactions, there are important exceptions. The resistance to either heat or mass transport may be sufficiently large so that one of these phenomena controls the overall rate. In this case, the bulk of the reaction mixture is always near a state of equilibrium and the contribution of the chemical reaction to the rate of the combined phenomena can be neglected.

Another complication usually found in industrial chemistry is the presence of undesirable secondary reactions accompanying the main reaction. Every effort is made to suppress competing secondary reactions when a chemical reaction is studied in the laboratory to determine the form of its rate equation, the value of its rate coefficients, or its mechanism. This is only natural, because competing reactions complicate the interpretation of experimental data. In an industrial environment, the same main reaction usually will be accompanied by one or more secondary reactions, which may occur in parallel or in series with the course of the main, desired reaction. Sometimes the secondary reactions may be natural alternatives to the main reaction. At other times the secondary reactions are due to causes theoretically subject to elimination, but economically tolerable. Examples of such causes are impurities in feed streams, inadvertent introduction of catalyst from the walls of the vessel, and imperfect temperature control.

The importance of secondary reactions relative to the main reaction is reflected in a quantity known as a chemical reaction efficiency.

This quantity has also been termed selectivity by Hougen and Watson (3). Consider the stoichiometric equation

$$\nu_A M_A + \nu_B M_B + \nu_C M_C + \cdots = \nu_N M_N + \nu_P M_P + \cdots \qquad (1)$$

where M_A, M_B, ... represent molecular weights of reactants, A, B, ..., M_N, M_P, ... represent molecular weights of products N, P, ..., and the ν's are stoichiometric coefficients. The chemical efficiency of A, χ_A, for this reaction is defined by

$$\chi_A = \frac{\nu_A \text{ (moles of N in reactor effluent - moles of N in feed)}}{\nu_N \text{ (moles of A in feed - moles of A in reactor effluent)}} \qquad (2)$$

The corresponding conversion per pass or per batch, W_A, and yield, Y_A, are given by

$$W_A = \frac{\text{moles of A in feed - moles of A in effluent}}{\text{moles of A in feed}} \qquad (3)$$

and

$$Y_A = \frac{\nu_A \text{ (moles of N in effluent - moles of N in feed)}}{\nu_N \text{ (moles of A in feed)}} \qquad (4)$$

The quantity χ reflects the efficiency of conversion of raw materials to desired products, and W reflects the size of the recycle stream. The economic importance of these quantities is obvious.

Denbigh (4) has called attention to another feature of industrial chemical reactions. He points to the advantage that can be obtained for a set of stirred reactors connected in series if the temperature of the reaction mixture is varied in the individual reactors so as to optimize

χ and W. Other operating conditions can be varied, and the idea is applicable to other types of reactors. In general, the deliberate variation of some operating condition, for example, heat exchange with the reaction mixture, may be called "programmed control" of the operating variable which, in the example given, is temperature.

The wide variety of industrial chemical reactions precludes the use of a single theoretical approach in all instances. This fact may be verified by an inspection of the current technical literature of the field. Although there is no completely general theory, some generality can be obtained by dividing industrial reactions into classes to which single theories may be applied. Two examples of systems of classifications are those of Walas (5) and Broetz (6). From these it can be seen that, among other things, the type of reaction vessel and the nature of the reaction mixture must be considered in such a system.

Theories of industrial chemical reactions are applied in different ways by engineers in the areas of process development, process design, and operation. For example, the problems of designing a reactor and predicting improved operating conditions for an existing reactor are superficially different. A theory or method of calculation developed for use with one problem may not be convenient to use with the other. However, the same information is involved in both problems, either as given data or as the required solution. This situation suggests that a theory suitable for one of the two problems must be related mathematically to any theory suitable for the other problem, although the relation may be complicated or obscure. Solution by trial is usually satisfactory where the direct application of a theory is awkward.

Theoretical Problems.--One of the central theoretical problems of chemical reaction engineering, as discussed in the preceding section, is the need to make predictions concerning a complex of simultaneous, mutually-interacting, chemical and physical phenomena. In making these predictions one encounters two obstacles: the coupling of chemical reactions with transport phenomena and the difficulty of solving the equations of change when non-linear expressions for the chemical reaction rate are introduced.

First of all, chemical reactions in industrial processes are usually coupled with transport phenomena. When this occurs, terms that express the generation of heat and the production of a molecular species must be included in the energy and continuity equations. Since these terms are both temperature and concentration dependent, neither equation can be solved alone; they must be solved simultaneously. This is why predictions concerning a combination of phenomena cannot be obtained by superimposing predictions for the individual phenomena. The coupling of transport phenomena with chemical reactions has been discussed in detail by Bosworth (7), Prager (8), and Bird, Stewart, and Lightfoot (9).

The second obstacle is also a mathematical difficulty. It is well known that non-linear equations are more difficult to solve than their linear analogs. Since accurate expressions for rates of chemical reactions are usually non-linear with respect to temperature or concentration, or both, the energy and continuity equations become non-linear when these expressions are introduced.

Sometimes the above obstacles may be removed from the mathematical formulation of the problem if a few judicious assumptions are made.

However, if one sacrifices an accurate mathematical description in order to gain solvability one incurs a risk that the solution for the simplified mathematical model will be a poor solution to the original problem.

Under many conditions of great practical importance the difficulties mentioned just above become pronounced. As two examples, the scale up of reactors on the basis of the theory of modelling and the use of programmed temperature control will be discussed.

The aim of the theory of modelling is to predict the behavior of a process in a large apparatus, called the prototype, from the behavior in a model.[1] It can be shown that, under certain conditions, the chemical compositions of the two reaction mixtures in model and prototype reactors will be equal at geometrically corresponding points. This condition is called chemical similarity. Since heat transport, mass transport, and the flow phenomena are coupled with the chemical reaction, similarity also must be obtained with respect to these phenomena before chemical similarity can occur. Damkoehler (1) has demonstrated that it is impractical to attempt to have similarity with respect to all of these phenomena at once. Even more important, the conditions that would produce chemical similarity for a main reaction, considered by itself, will rarely yield chemical similarity for its accompanying secondary reactions. As a result, the chemical efficiencies and conversions obtained in the prototype reactor may differ by unexpected amounts from those of the model. This is an important consequence because of the economic

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[1]The terminology used in this discussion of modelling theory is that of Johnstone and Thring (75).

significance of chemical efficiencies and conversions in industrial processes.

The theoretical advantage of optimally programmed temperature control over arbitrary, non-optimum control is unquestioned. But here the coupling of heat transport with the chemical reaction is again a complication. If heat is generated or absorbed by a chemical reaction, there is always some internal heat transport, even when the reactor is operated adiabatically. A program of temperature control introduces additional heat transport, and this increases the difficulty of making accurate predictions of the behavior of the combined phenomena. In cases where accurate predictions of behavior cannot be made, the optimum program of control cannot be predetermined and the economic advantage of the optimum program over another, arbitrary program will be unknown.

Objectives and Limitations.--The general objective of this research is to provide an improved method for predicting the behavior of those industrial reactions in which there is an important coupling of transport phenomena with the chemical reaction. This method would permit the prediction of conversions and chemical efficiencies for a given program of temperature control. The method would also allow the effect of a change of scale to be predicted in the absence of chemical similarity between model and prototype reactors.

Since the general theory of industrial chemical reactions is not feasible, as mentioned earlier, the general objective is sought for only one class of reactions and only one class of reactors: homogeneous reactions in continuous-flow, tubular reactors. This investigation also is

limited to steady state operation, turbulent flow, and reaction mixtures having essentially constant physical properties. Two heat transfer conditions are considered. These are, first, a fixed pattern of wall temperatures and, second, heat exchange between the reaction mixture and the fluid in an external jacket.

The restriction of this study to reaction mixtures having essentially constant physical properties is undesirable, because changes in viscosities and densities are frequently large in industrial chemical reactions. This restriction is a necessary one, however. The prediction of the effects of property variations on flow phenomena is an unsolved problem at the present time. In studies of heat exchange between fluids and solid surfaces, useful results have been obtained in spite of the assumption of constant fluid properties. This fact suggests that the method of this investigation will be useful in many cases that are nominally excluded by the assumptions. However, the method should not be expected to apply to reactions in which there are large density variations, for example, in the dehydrogenation of hydrocarbons. Nor should it be expected to apply to cases in which large viscosity variations occur, for example, in liquid phase polymerizations.

There are three more limitations of a different nature to which the attention of the reader must be directed. The first limitation is that the theoretical part of this investigation gives a demonstration of method rather than a general solution. This is discussed further in the next section. In addition, the method, which is based on numerical analysis, involves such a large amount of computation that its use is

practically limited to those readers who have available large, high-speed, digital computers. The third limitation, the consideration of only a single reaction, was adopted to reduce the required computer time. However, it is anticipated that, in practice, the computer program used here could be modified to include secondary reactions.

The Plan of the Investigation.--This investigation may be divided into two distinct parts, one theoretical and one experimental.

For the theoretical part of this investigation, a tubular reactor is described by the energy equation, the continuity equations for reactants, an equation for the temporal-mean velocity distribution and associated boundary conditions. This description constitutes a boundary value problem in mathematics. The forms of the equations and boundary conditions and the assumptions made in their derivation may be found in Chapter III.

Numerical analysis is employed in solving the boundary value problem since this technique is relatively unaffected by the non-linearity of the problem. First, the derivatives that occur in the equations of change and in the boundary conditions are replaced by finite difference approximations to give an approximate boundary value problem. Then, this approximate boundary value problem is solved for particular values of its parameters and initial conditions.

The products of the theoretical part of this investigation are a method of numerical analysis for the boundary value problem of a tubular reactor and some particular solutions which illustrate the results obtainable by this method. These results do not constitute a general

solution in the mathematical sense. In simple cases, the numerical solutions may be generalized by an empirical correlation of the particular solutions as a function of the parameters of the problem. In the present problem there are ten of these parameters, so such an empirical correlation would have been difficult to obtain and cumbersome to use.

The experimental part of this investigation is intended to provide data for comparison with theoretical results and to test some assumptions on which the theoretical formulation of the problem is based. Velocity, temperature and concentration distributions are obtained in a jacketed, tubular reactor, one inch in diameter and fifteen feet tall. The reaction used in this experimental work is the aqueous saponification of methyl acetate by sodium hydroxide. The ranges of the operating variables covered in the experiments are Reynolds numbers from 4,500 to 10,000, initial concentrations from zero to one mole per liter and jacket temperatures from 0°C to 40°C in excess of initial temperatures.

CHAPTER II

REVIEW OF PREVIOUS CONTRIBUTIONS

The literature reviewed in this chapter is divided into five sections: flow phenomena, heat and mass transport, modelling theory, models of tubular reactors, and mathematics.

Flow Phenomena

The theoretical approach used in this investigation required an accurate representation of turbulent flow and transport phenomena; for this reason, careful attention to the details of these subjects was essential. First of all, some of these details are considered in order to provide a basis for discussion. Then, previous work on distributions of temporal-mean velocity and eddy diffusivity of momentum in flow through pipes is reviewed. Finally, the contributions that form the bases for the axial diffusion and the autoclave-series models of tubular reactors are considered. The discussion of flow phenomena given here is not intended to be comprehensive; for further information, the reader is referred to an excellent review article by Sherwood (10) and to the books of Knudsen and Katz (11) and Hinze (12).

Basis for Discussion.--The eddy diffusivity of momentum, ε_v, for constant fluid properties and steady flow is defined by

$$\frac{\tau\, g_c}{\rho} = (\nu + \varepsilon_v)\frac{du}{dy} \tag{5}$$

where τ is the shear stress at a surface parallel to the pipe wall, ν is the kinematic viscosity, u is the temporal-mean velocity parallel to the wall, ρ is the fluid density, and y is displacement from the wall in the direction of the normal. Since a force balance shows that τ is proportional to radius for flow in pipes, this equation may be written

$$\frac{\varepsilon_y}{\nu} = \frac{\frac{\tau_w g_c r}{\nu \rho r_w}}{\frac{du}{dy}} - 1 = \frac{s}{\frac{du^+}{dy^+}} - 1 \qquad (6)$$

where τ_w is the shear stress at the pipe wall, r_w is the radius of the wall, $s = r/r_w$, $u^+ = u/\sqrt{\frac{\tau_w g_c}{\rho}}$, and $y^+ = \left(\frac{y}{r_w}\right) \frac{r_w}{\nu} \sqrt{\frac{\tau_w g_c}{\rho}}$.

These equations, 5 and 6, show how the distribution of ε_y is related to the distribution of u.

In the field of flow phenomena there is a notable lack of agreement among the authorities as to the values of various quantities that are obtained from experimental measurements. For examples, the reader may compare the velocity distributions of Sleicher (13) and Laufer (14) and the eddy diffusivity distributions of Reichardt (15) and Rothfus, Archer, and Sikchi (16). The importance of these problems and the high quality of the numerous investigations of them demand explanations for the existing disagreements.

There are at least three causes for lack of agreement concerning distributions of velocity and eddy diffusivity of momentum. Naturally, differences in equipment and experimental technique cause some variability

between the experimental data from different investigations. Besides this, there are variations in the interpretation of the data. And in the opinion of the writer, the variability of experimentally measured velocities within a single investigation is generally underestimated. That is, the measurements are treated as if they were much more reproducible than they are in fact.

An example of variation in the interpretation of data is found in the correction of experimental impact pressure and displacement data. Corrections have been suggested to compensate for transverse velocity gradients, viscous effects, and turbulent velocity fluctuations; but procedures for such corrections vary widely. Often, one or more of these corrections is omitted altogether. The reader is referred to Knudsen and Katz (17), Laufer (18), and Macmillan (19) for information on the specific corrections that have been used by various investigators and for further references.

To illustrate the variability of experimental velocity data, three sets of the data of Sleicher (13) were combined and subjected to a statistical analysis. Details of this analysis will be found in Appendix I. These three sets of data were obtained at Reynolds numbers of 39,000, 39,100, and 40,000, so that little of the variability of these data can be attributed to differences in Reynolds number.

The results of the analysis are given in Table 1. An examination of the first row of this table shows a 95 per cent confidence interval of 0.76 for u^+, or about five per cent of the estimated value of u^+, 15.15. The same data yield a 95 per cent confidence interval of 9.4 for ε_v / ν, or about 34 per cent of the estimated value of ε_v / ν.

Table 1. Results of a Statistical Analysis of Typical Velocity Data

y^+	u^+ (Sleicher's Fig. 3)	Deg. of Freedom	Estimates of		
			$u^+ \pm$ (95% C.L.)	$\frac{du^+}{dy^+} \pm$ (95% C.L.)	$\varepsilon_v/\nu \pm$ (95% C.L.)
67.4	15.5	10	15.15 ± 0.38	0.0340 ± 0.0058	26.5 ± 4.7
239.9	18.95	17	18.83 ± 0.39	0.0132 ± 0.00081	58.5 ± 3.6
516.2		14	21.36 ± 0.43	0.00667 ± 0.00062	74.7 ± 7.0
65.7	15.45	34	15.35 ± 0.69	0.0395 ± 0.0059	22.6 ± 3.5

This illustrates the fact that the relative variability of eddy diffusivities is inherently greater than the relative variability of the velocity data from which the eddy diffusivities were computed. If the sample variances of u^+ in this analysis are assumed to be independent of sample size, and the data points are assumed to be uniformly distributed over the range of y^+, the effect of more of fewer velocity data can be seen. Consider the third row and suppose that only six experimental velocities had been available instead of sixteen. Then the confidence interval for u^+ would become 0.98 since the sample variance was unchanged. However, the confidence intervals of du^+/dy^+ and ε_v/ν would be increased to 0.0024 and 28, respectively, because the variances of these quantities are roughly proportional to $1/(2n+3)$ where n is the number of experimental measurements. Under the same assumption, if n were increased from 16 to 503, the confidence interval for ε_v/ν would be 0.75, or about one per cent of the present estimate of ε_v/ν.

The fourth row shows the result when data from all eleven of Sleicher's sets were included in the analysis. If the variance of u^+ had remained the same as in the first row of the table, a reduction in the confidence interval of ε_v / ν would have been expected from the increase in n. However, variations in the Reynolds number of the eleven data sets caused an increase in the variance of u^+. Consequently, the length of the confidence interval relative to the size of ε_v / ν is about the same as in the first row. Now, consider the second row and suppose that the measurements could be made with more precise equipment and under more closely controlled conditions so that the variance of u^+ would be reduced. The confidence interval of u^+ would have to be reduced from 0.78 to 0.064 in order to reduce the confidence interval of ε_v / ν to one per cent of the present estimate of ε_v / ν.

Sleicher's work was chosen for the above analysis because the data available for a single Reynolds number were sufficiently numerous to permit reliable statistical estimates. Judging from the scatter of data points around published "mean curves," it seems likely that the variability of the velocity data from most investigations is at least as great as Sleicher's. The analysis shows the difficulty in obtaining precise values of eddy diffusivity from velocity data. In view of this difficulty, at the present time the exact relationship between ε_v / ν and r / r_w should not be considered to have been established by experiment.

More than a dozen correlations have been proposed for the temporal-mean velocity distribution for flow through pipes. In order to assess the relative values and the limitations of these correlations,

it is necessary to establish some criteria. The seven criteria set forth below afford a reasonable basis for comparing the merits of various correlations.

1. A velocity correlation should not conflict with experimental velocity profiles. However, as explained in the preceding paragraphs, the variability between investigations and the variability within the data of a single investigation permit different correlations to satisfy this criterion without being identical. For experimental velocity data, the reader is referred to the work of Stanton (20), Stanton and Pannell (21), Nikuradse (22), Fage (23), Reichardt (24), Laufer (14), Deissler (25), Rothfus, Monrad, and Senecal (26), Senecal and Rothfus (27), Nunner (28), Sleicher (13), Macmillan (19), Weissberg (29), and Isakoff and Drew (30).

2. The correlation should be consistent with respect to the bulk velocity. In other words, the value of $\bar{u}$ computed from a velocity distribution, $u(s)$, by

$$\bar{u} = 2 \int_0^1 s\, u(s)\, ds$$

should equal the value of $\bar{u}$ given explicitly or implicitly by the original data used to calculate $u(s)$.

3. A correlation should show the influence of Reynolds number, if it is intended to be used over a range of Reynolds numbers. For a constant y^+, u^+ varies with Reynolds number, or, formally,

$$\left(\frac{\partial u^+}{\partial N_{Re}}\right)_{y^+ = \text{const.}} \neq 0$$

This can be seen in the data presented by Rothfus and Monrad (31) for Reynolds numbers below 10,000. The effect of Reynolds number on u^+ is commonly supposed to be negligible for Reynolds numbers greater than 20,000. However, the precise, impact-tube data of Macmillan (19) show that the effect is measurable for Reynolds numbers as great as 80,000.

4. The ratio of bulk to maximum velocity should agree with experimental data. Many measurements of this ratio have been made by a number of investigators and the agreement between them is generally good. Robertson (32) and Rothfus, Archer, and Sikchi (16) present correlations of collections of $\bar{u}/u_{max}$ data.

5. The derivative, du/dy, obtained from the correlation should vanish at $r = 0$, because the shear stress, τ, is zero at this point.

6. The velocity and the first derivative should be continuous functions of r/r_w for the entire range $0 \leq r/r_w \leq 1$. This insures that ε_v/ν will also be continuous, if it is calculated from equation 6. There is no experimental support for discontinuities in either u or du/dy. For the sake of physical simplicity, the writer assumes that these quantities are continuous functions of r/r_w.

7. The order of magnitude of the eddy diffusivity of momentum computed from the correlation at $r = 0$ should be the same as the orders of magnitude of experimental eddy diffusivities of heat and mass at $r = 0$. For the range of r/r_w where du/dy may be estimated from experimental data, ε_v, ε_H, and ε_m have been found to have the same order of magnitude. In addition, experiments show that neither ε_m or ε_H approach zero at the axes of pipes or channels. The writer

can see no basis for supposing that one of these quantities vanishes where the other two do not, particularly since all three reflect transport phenomena with a common origin, that is, turbulent flow.

Results concerning the relative magnitudes of ε_v and either ε_H or ε_m can be found in the work of Sherwood and Woertz (33), Page, Schlinger, Breaux, and Sage (34), Sleicher (13), Dhanak (35), and Abbrecht and Churchill (36). In addition, values of ε_H and ε_m for the central portion of the flow were determined by Baldwin and Walsh (37) and Flint, Kada, and Hanratty (38), respectively. Other arguments on this question are advanced by Prandtl (39), Lynn and Rothfus (40), and Brooks and Berggren (41).

Velocity and Eddy Diffusivity Correlations.--Eight expressions for temporal-mean velocity distributions are considered here. These correlations are certainly not the only important ones. They were chosen to illustrate the different variants available. In addition, four correlations of the eddy diffusivity of momentum are discussed.

The velocity correlation that is best known and most widely used is the so-called "universal" velocity distribution of von Kármán (42). This consists of the three equations,

$$u^+ = y^+, \qquad 0 \leq y^+ \leq 5,$$

$$u^+ = -3.05 + 5.0 \ln y^+, \qquad 5 < y^+ \leq 30, \tag{7}$$

and

$$u^+ = 5.5 + 2.5 \ln y^+, \qquad 30 < y^+ .$$

This expression does not conflict greatly with experimental data for Reynolds numbers greater than 10,000. However, when the experimental

velocity data for a single Reynolds number are drawn on a graph having coordinates of u^+ and log y^+, the resulting profile is seen to have a noticeable ogee-like shape in the range $40 < y^+ < y^+_{max}$. The profile has a positive slope throughout, but is concave upwards in its central part and concave downwards in a small portion near its upper end. These characteristics are present in the hot-wire anemometer data of Sleicher (13) and of Weissberg (29), the ultra-microscope data of Fage (23), and the impact-tube data of Laufer (14) and Macmillan (19).

This correlation is fairly consistent with respect to $\bar{u}$, but naturally it is poor in this respect for Reynolds numbers less than 10,000 because the effect of Reynolds number on u^+ at constant y^+ is neglected. The ratio of computed $\bar{u}$ to the original $\bar{u}$ was found by the writer to be about 0.952, 0.988, and 1.006 at Reynolds numbers of 5,000, 10,000 and 40,000, respectively. The ratio of $\bar{u}/\bar{u}_{max}$ is significantly greater than the best experimental data. The experimental values of Nikuradse (22) of $\bar{u}/u_{max}$, as published, are in fair agreement, but Ross's (43) reanalysis of these data puts the experimental points well below the line given by this correlation. The derivative, du/dy, is non-zero at $r = 0$; and this requires ε_v to vanish at this point. Finally, du/dy is discontinuous at $y^+ = 30$; and, of course, ε_v is also discontinuous here.

Deissler (44) improved on equations 7 by using a single equation for the range $0 \leq y^+ < 26$. His equations are

$$u^+ = \int_0^{y^+} \frac{dy^+}{1 + (0.124)^2\, u^+y^+\{1 - \exp[-(0.124)^2\, u^+y^+]\}}, \quad 0 \leq y^+ < 26$$

and (8)

$$u^+ = 3.8 + 2.78 \ln y^+, \quad 26 \leq y^+$$

Equations 8 conflict less with experimental data than equations 7 within a range of Reynolds numbers from 15,000 to 100,000. The ratio of computed $\bar{u}$ to original $\bar{u}$ was found by the writer to be about 0.965 and 1.00 at Reynolds numbers of 10,000 and 40,000, respectively. The effect of Reynolds number of u^+ is neglected. The agreement with experimental $\bar{u}/u_{max}$ data is better than equations 7 for Reynolds numbers greater than 10,000 and poorer for smaller Reynolds numbers. At $r = 0$, du/dy fails to vanish, so ε_v must be zero at this point. As Sherwood (10) shows, du/dy is discontinuous at $y^+ = 26$.

Ruth and Yang (45) developed an equation

$$u^+ = 2.92 + 5.7 \log\{y^+_{max}[e^{1.5(1 - s^{3/2})} - 1]\}, \quad 30 < y^+ \tag{9}$$

that correctly shows the effect of Reynolds number on u^+. However, this equation is intended for use only in the turbulent "core" of the flow and only for Reynolds numbers greater than 100,000.

Rannie (46) proposed the equations

$$u^+ = 14.53 \tanh(0.0688\ y^+), \quad 0 < y^+ < 27.5$$

and (10)

$$u^+ = 5.5 + 2.5 \ln y^+, \quad 27.5 \leq y^+.$$

These have the advantage of a continuous derivative over the entire range of y^+. Otherwise, the comments concerning equations 7 apply.

Van Driest (47) developed the equation,

$$u^+ = \int_0^{y^+} \frac{2\, dy^+}{1 + \{1 + 4(0.4)^2(y^+)^2[1 - \exp(-y^+/27)]^2\}^{\frac{1}{2}}}, \quad 0 \leq y^+ < 60 \tag{11}$$

and used $u^+ = 5.5 + 2.5 \ln y^+, \quad 60 \leq y^+.$

The velocity, u^+, and the derivative, du^+/dy^+, are practically the same for both equations at $y^+ = 60$, so that these equations also have the advantage of a continuous first derivative over the entire range of y^+. Besides, Van Driest's formulation appears to agree better with most experimental data than equations 10 for $10 < y^+ < 30$ and for Reynolds numbers above 15,000. Equation 11 was derived under the assumption of constant shear stress. Franklet (48) and Gill and Scher (49) modified this equation to account for the linear relation between shear stress and radius. The modified equation may be written

$$u^+ = \int_o^{y^+} \frac{2(1 - y^+/y^+_{max})dy^+}{1 + \left\{1 + 4(y^+_{max})^2(\ell_p/r_w)^2(1 - y^+/y^+_{max})\right\}^{\frac{1}{2}}} \qquad (12a)$$

where ℓ_p is the Prandtl mixing length, defined by

$$\frac{\tau g_c}{\rho} = \nu \frac{du}{dy} + \ell_p^2 \left(\frac{du}{dy}\right)^2 \qquad (12b)$$

Hefner (50) proposed the equations

$$u^+ = \int_o^{y^+} \frac{2(1 - y^+/y^+_{max})}{1 + \left\{1+4(0.4)^2(y^+)^2[1-\exp(-0.037y^+)]^2(1-y^+/y^+_{max})\right\}^{\frac{1}{2}}} \quad , \qquad (13a)$$

$$0 \leq y^+ < 70 \ .$$

and

$$u^+ = 2.1730 - \frac{1}{\ln N_{Re} - 7} + 2.778 \ln N^*_{Re} +$$

$$(2.766 + 0.0013 \ln N^*_{Re})[\ln(y/r_w) - 0.10(y/r_w)^{10}] \ , \qquad (13b)$$

$$70 \leq y^+, \quad N^*_{Re} = N_{Re}\sqrt{f/2} \ .$$

These equations retain the advantage of a practically continuous first derivative over the entire range of y^+. At $r = 0$, du/dy vanishes, and ε_v computed from equation 13b is non-zero at $r = 0$. In addition, the dependence of u^+ on Reynolds number for constant y^+ is correctly shown for Reynolds numbers greater than about 20,000. The agreement of this correlation with experimental $\bar{u}/u_{max}$ data is poor for Reynolds numbers below 40,000, and the conflict with experimental profile data becomes noticeable at Reynolds numbers below 20,000. The consistency with respect to $\bar{u}$ has not been examined, but is presumed to be good for Reynolds numbers greater than 40,000. The reader should note that equation 13a is equivalent to 12a with

$$\frac{\ell_p}{r_w} = 0.4 \frac{y}{r_w} [1 - \exp(-0.037y^+)] \qquad (13c)$$

Gill and Scher (49) proposed the use of equation 12a over the entire range of y^+ with

$$\frac{\ell_p}{r_w} = 0.36 \frac{y}{r_w} [1 - \exp(P_G y/r_w)] , \qquad (14)$$

$$P_G = -\frac{y^+_{max} - 60}{22}$$

This correlation has a number of advantages. First of all, the first derivative of u is continuous for the entire range of y^+ and vanishes at $r = 0$. However, du/dy does not approach zero rapidly enough as r approaches zero, so ε_v vanishes at $r = 0$. The influence of Reynolds number on u^+ is accounted for and, as Gill and Scher point

out, their velocity distribution reduces to the Hagen-Poiseuille equation at a Reynolds number of 1,800. Unfortunately, there are also a number of defects in this correlation. The most serious of these is the conflict with experimental data for Reynolds numbers above 5,000 and $y^+ > y^+_{max}/2$. This is seen again in the extreme disagreement with experimental values of $\bar{u}/u_{max}$ at Reynolds numbers greater than 3,000. In view of these conflicts with experimental data, consistency with respect to $\bar{u}$ cannot be expected for Reynolds numbers greater than 5,000.

Rothfus and Monrad (31) showed that the effect of Reynolds number on u^+ can be accounted for approximately by using the variables $u^{++} = u^+ \frac{\bar{u}}{u_{max}}$ and $y^{++} = y^+ \frac{u_{max}}{\bar{u}}$. When experimental data points for a range of Reynolds number are drawn on a graph having u^{++} and log y^{++} coordinates, the points are much less dispersed than when presented on a graph having coordinates of u^+ and log y^+. The slight ogee-like shape that experimental velocity profiles have when they are represented on a semi-logarithmic graph has been mentioned in connection with equations 7. Since the end points of the profiles, that is, the points where $y^{++} = y^{++}_{max}$, depend on Reynolds number, a complete coincidence of profiles for a range of Reynolds number cannot be obtained by the transformation proposed by Rothfus and Monrad. In addition, they point out that this transformation forces a noticeable separation between the velocity distributions for large and small Reynolds numbers in the range $y^+ < 5$.

Rothfus, Archer, and Sikchi (16) presented graphs of eddy diffusivity and mixing length distributions. They drew smooth curves to

represent the experimental velocity data and obtained derivatives from the slopes of these curves. These authors should be applauded for what they attempt to do, but their results are open to two criticisms. The first stems from their reliance on Nikuradse's 1932 paper (22) for velocity data in the range of Reynolds numbers from 4,000 to 3,000,000. Ross (43) and Brooks and Berggren (41) have objected to Nikuradse's treatment of his data, but these objections appear to have been overlooked by Rothfus and co-workers. If this is the case, the objections would apply to the graphs of these authors, as well. The second criticism concerns the precision of quantities computed from imprecise, experimental data. It was shown in the preceding section that precise, objective estimates of du/dy cannot be made from experimental velocity data, unless these data are both precise and numerous. It is questionable whether the quality and quantity of the data used by Rothfus and co-workers are sufficient for their purpose. For one example, the variability of the two profiles reported by Senecal and Rothfus (27) at a Reynolds number of about 4,100 may be estimated from internal evidence. The comparison between these data and those of Sleicher that were analyzed in the preceding section is unfavorable to the work of Rothfus and Senecal. Under the circumstances, it is not known whether the confidence intervals associated with the curves of Rothfus, Archer, and Sikchi should be on the order of 10 per cent or 100 per cent of the computed quantities. If the latter is true, the curves of these authors can hardly represent anything more than general trends.

Corcoran, Opfell, and Sage (51) presented a tabulation of eddy diffusivities for a range of Reynolds numbers from 5,000 to 100,000.

The entries in this table were computed from the equations,

$$u^+ = \frac{1}{0.0695} \tanh(0.0695y^+), \quad 0 \leq y^+ < 27$$
$$u^+ = 5.5 + 2.5 \ln y^+, \qquad 27 \leq y^+ \tag{15}$$

These authors stated that "The relative viscosities presented for Reynolds number below 20,000 are not strictly applicable inasmuch as the empirical constants were evaluated primarily from information on air streams with the Reynolds numbers greater than this value." It was pointed out in connection with equations 7 that there is a slight ogee-like shape to experimental velocity profiles when they are drawn using semi-logarithmic coordinates. This fact prevents the second equation of 15 from being an accurate representation of a velocity profile and makes the status of this tabulation of eddy diffusivity uncertain.

Reichardt (15) suggested the expressions,

$$\frac{\varepsilon_v}{\nu} = 2.7 \times 10^{-5} (y^+)^5, \qquad 0 \leq y^+ < 6$$
$$\frac{\varepsilon_v}{\nu} = 0.4[y^+ - 11 \tanh(\frac{y^+}{11})], \quad 6 \leq y^+ < 30 \tag{16}$$
$$\frac{\varepsilon_v}{\nu} = \frac{0.4y^+_{max}}{3} [0.5 + (r/r_w)^2][1 - (r/r_w)^2], \quad 30 \leq y^+$$

on the basis of experimental heat transfer data. He showed that these equations yield a velocity distribution that does not contradict the experimental data for $0 \leq y^+ \geq 50$.

Tien (42) derived the equation

$$\varepsilon_v = 3.3(y^+)^{0.25} \frac{r_w}{0.6} [0.43 - 0.5(y/r_w - 0.5)^2] \qquad (17)$$

He showed that $\varepsilon_v = \varepsilon_H$ for an ideal fluid having constant density, provided that effects due to molecular viscosity and conductivity are negligibly small, and that the velocity and temperature gradients normal to the wall are constant.

Bases for Two Reactor Models.--Brief mention must be made of work which underlies the axial-diffusion and autoclave-series models of tubular reactors.

In 1948, Bosworth (53) published a paper dealing with residence times for laminar flow in tubular reactors. The following year, he(54) extended this work to include turbulent flow. For laminar flow, Bosworth concluded that molecular diffusion in the radial direction has a negligible effect on the residence-time distribution provided that

$$r_w > 13 \sqrt{\frac{D_m L}{\bar{u}}} \qquad (18)$$

and

$$L > 6.5 \times 10^4 \, D_m / \bar{u} \qquad (19)$$

He pointed out that these conditions are rarely possible for gases in laminar flow, but are usually satisfied for liquids. In the companion paper on turbulent flow, he concluded that there are no conditions under which radial diffusion has a negligible effect on the residence-time distribution.

Danckwerts (55) considered residence-time distributions in general and pointed out that a knowledge of the residence-time distribution permitted rigorous reactor calculations only in the case of first-order reactions.

Taylor (56, 57) showed that a combination of radial velocity gradient and radially-directed diffusion produces a virtual axial diffusion of the bulk concentration in fluid flow through pipes. In addition, he obtained expressions for the virtual axial diffusivity in laminar and turbulent flow and then supported his results with experimental data. Taylor found that in laminar flow

$$D_T = \frac{r_w^2 \bar{u}^2}{48 D_m} \tag{20}$$

provided that

$$\frac{L}{\bar{u}} >> \frac{r_w^2}{7.2 D_m} \tag{21}$$

For turbulent flow, he found that

$$D_T = 10.1\, r_w\, u^* \tag{22}$$

Experimental measurements of D_T tend to be somewhat larger than the values predicted by Taylor for small Reynolds numbers in the turbulent range. For this reason, Tichacek, Barkelew, and Baron (58), following Taylor's theory, used experimental velocity profiles to determine curves of $D_T/(2r_w\bar{u})$ versus $4f_F$ for both gases and liquids. The resulting curves show improved agreement with data from pipeline mixing experiments.

Using frequency response techniques, Kramers and Alberda (59) show that a set of series-connected, continuous-flow mixing vessels may be used to approximate the residence-time distribution of piston flow and superimposed axial diffusion. In view of Taylor's investigations mentioned above, this provides a rational basis for the use of a mathematical formulation based on a series of well-mixed autoclaves as a model for turbulent flow in a tubular reactor.

Heat and Mass Transport

Accurate means of calculating concentration and temperature profiles are needed to consider non-isothermal reactions. In the present problem, accurate predictions of these distributions require knowledge of the transport coefficients of heat and mass in turbulent flow. These quantities are empirical in nature and bear some relation to the eddy diffusivity of momentum. This relation appears to be affected by the Reynolds number of the flow and the Prandtl number of the fluid. The picture becomes even more complicated when one considers that the temperature and concentration gradients associated with the transport of heat and mass affect the molecular properties of the fluid and thus the velocity distribution. In view of these complications, it is not surprising that transport phenomena in turbulent flow are not completely understood. The existing theories and experimental facts are well summarized by Hinze (12) and Sherwood (10).

In the present review, emphasis is placed on the sources of the diffusivities of heat and mass used by other investigators and on the ways in which the various complications have been handled.

Deissler (44) assumes that the eddy diffusivity of momentum can be expressed by

$$\frac{\varepsilon_v}{\nu} = (0.124)^2 u^+ y^+ \{1 - \exp[-(0.124)^2 u^+ y^+]\}, \quad 0 \leq y^+ < 26 \tag{23a}$$

and

$$\frac{\varepsilon_v}{\nu} = 0.36 \left[\frac{du^+}{dy^+}\right]^3 \Big/ \left[\frac{d^2u^+}{d(y^+)^2}\right]^2, \quad 26 \leq y^+ \tag{23b}$$

The constants in these expressions were evaluated from Deissler's (25) experimental velocity data for isothermal flow. He first showed that the above expressions do not conflict with these experimental velocity data by integrating to obtain curves of u^+ versus y^+. Then he assumed that $\varepsilon_H / \varepsilon_v = 1$, independent of Reynolds number and Prandtl number. For fluids having constant physical properties and for fully developed transfer, he obtained generalized temperature and concentration profiles for various Prandtl or Schmidt numbers from 0.73 to 3,000. Charts based on these profiles relate the Nusselt and Stanton numbers to the Reynolds number and either the Prandtl or Schmidt number of the fluid. These relations were shown to be consistent with the results of gross heat and mass-transfer experiments, that is, experiments where the relevant transfer coefficients were determined, but the profiles were not. Friend and Metzner (60) claim that Deissler's results for large Prandtl numbers are in error by 15 to 20 per cent. In any event, the agreement between Deissler's theory and gross transfer experiments does not provide a conclusive confirmation of his generalized profiles and eddy diffusivity expressions. As discussed by Sherwood (10), other

investigators have obtained approximately the same results using other assumptions concerning eddy diffusivities.

Deissler also considers heat and mass transfer in fluids having variable properties. He replaces equation 23a by

$$\frac{\varepsilon_v}{\nu} = (0.124)^2 u^+ y^+ \{1 - \exp[-(0.124)^2 u^+ y^+ (\mu_w/\mu)]\} , \qquad (23c)$$

$$0 \leq y^+ < 26$$

for liquids (variable viscosity, constant density) and

$$\frac{\varepsilon_v}{\nu} = (0.124)^2 \frac{u^+ y^+ \rho}{\rho_w} \{1 - \exp[-(0.124)^2 u^+ y^+ \nu_w/\nu]\} , \qquad (23d)$$

$$0 \leq y^+ < 26$$

for gases (variable viscosity and density). These equations are used to predict velocity and temperature distributions for various values of a dimensionless parameter β_D. This parameter is related to the heat flux density at the pipe wall.

Deissler's velocity profiles for liquids can be shown to be inconsistent. For example, consider a liquid flowing through a pipe, one section of which is heated and another unheated. Using Deissler's Figure 8, one can obtain velocity profiles for both sections. Suppose the fluid is water and that the mass flow rate and diameter are the same at both sections. At the unheated section of pipe, let $\bar{u} = 30$ cm./sec., $(N_{Re})_w = 40{,}000$, $T_w = 50°F$ and $\beta_D = 0$. Then, at the heated section, let $T_w = 86°F$ and $\beta_D = +0.002$. This gives $(N_{Re})_w = 65{,}000$ at the

heated section. The bulk velocities calculated from the distributions given by Deissler's Figure 8 are 30.0 cm./sec. and 27.9 cm./sec. for the unheated and heated sections of pipe, respectively. Although this inconsistency indicates that Deissler's analysis is poor for predicting profiles, it probably is satisfactory for its intended purpose, that is, predicting heat transfer coefficients.

Reichardt (24) discusses the effect on the velocity distribution of the variation in physical properties due to a temperature gradient. He considers a characteristic velocity, u_R^+, that separates the viscous layer of flow near a wall from the turbulent core of an incompressible fluid when the friction velocity, $u^* = [\tau_w g_c / \rho]^{\frac{1}{2}}$, is considered constant. The velocity, u_R^+, is not affected by a variation in the physical properties of the fluid in the viscous layer. Thus, the effect of a viscosity variation due to a temperature gradient is a change in the thickness of the viscous layer.

In a later publication, Reichardt (61) discusses the ratio, $\varepsilon_H / \varepsilon_v$. The experimentally determined values of this ratio have been found to be about 2 in free turbulence; but the average value in boundary layers is less, and values of 1.3 have been obtained for air flow. Reichardt believes that $\varepsilon_H / \varepsilon_v$ approaches unity as the Prandtl number approaches infinity, and that $\varepsilon_H / \varepsilon_v$ is a function of y/r_w which has its maximum at the pipe center line and decreases toward the wall.

Reichardt's ideas are based on the behavior of jets and wakes and the reader should note that they are in sharp contrast to the ideas

of Page, et al. (34), Sleicher (13), Jenkins (62), Rohsenow and Cohen (63), and Lykoudis and Touloukian (64). The ideas of these investigators are summarized by Sherwood (10). In addition, the discussions following the papers of Sleicher and Lykoudis and Touloukian present interesting, divergent viewpoints concerning the value and variation of $\varepsilon_H / \varepsilon_v$.

Sleicher (13) measured velocity and temperature distributions for heat transfer to air in well-developed, turbulent flow and calculated both ε_v and ε_H profiles from these data. He then used an electronic analog computer to obtain the eigenvalues and eigenfunctions of a series solution to the energy equation,

$$u \frac{\partial T}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left[r \left(\frac{\nu}{N_{Pr}} + \varepsilon_H \right) \frac{\partial T}{\partial r} \right], \qquad (24)$$

from the profiles. No changes in velocity distributions due to temperature gradients were detected in Sleicher's experiments. The ratio, $\varepsilon_H / \varepsilon_v$, calculated by Sleicher from his experimental data, was found to be dependent on r_w and Reynolds number. The values of $\varepsilon_H / \varepsilon_v$ for $y / r_w > 0.4$ ranged from 1.07 to 1.23 for Reynolds numbers of 80,300 to 14,500. For $y / r_w < 0.4$ and all Reynolds numbers, $\varepsilon_H / \varepsilon_v$ increased in the direction of the pipe wall and approached values between 1.4 and 1.5 in the vicinity of the wall.

Page, Corcoran, Schlinger, and Sage (65) and Page, Schlinger, Breaux, and Sage (34) reported experimental measurements of velocity and temperature distributions for heat transfer to air flowing between parallel plates. Eddy diffusivity distributions were calculated from

these data. Heat flux densities were varied from 0.0 to 0.116(BTU)(ft.)$^{-2}$(sec.)$^{-1}$ and mean temperature gradients (between plates) from 0 to 510(°F)(ft.)$^{-1}$. The effects of temperature gradients on the velocity distributions were found to be negligible in these experiments. The trends of the calculated values of $\varepsilon_H / \varepsilon_v$ agreed with those found by Sleicher.

Siegel and Sparrow (66) presented the eigenvalues of a series solution to the problem of heat transfer and internal heat generation for turbulent flow of fluid through a pipe. They chose representations of the distributions of velocity and eddy diffusivity of momentum that are similar to those of Deissler (44). This analysis assumes that the fluid properties are constant and that $\varepsilon_H / \varepsilon_v = 1$. The authors state that the reported results apply only to ". . . heat sources which are uniform across the tube cross section. However, the results can be extended to heat sources which may vary in the radial direction." The radial variation of heat sources may be arbitrary, but the strength of the source must be known prior to calculation as an explicit function of radius. The method does not apply to the problem of this study, where the rate of heat generation is an explicit function of temperature and concentration, and is an implicit function of radius.

In 1939, Sherwood and Woertz (33) reported the results of experiments in which mass was transferred from a falling film of water, through a countercurrent gas stream, to a falling film of calcium chloride brine. Concentration and velocity distributions were obtained and eddy diffusivities of momentum and mass were computed from these. Sherwood and

Woertz found that the slope of the concentration distribution curve was approximately constant in the central portion of the air flow, so they used an "average" slope to obtain an "average" value of ε_m. The ratio, $\varepsilon_m / \varepsilon_v$, found by these investigators was about 1.4.

Schwarz and Hoelscher (67) reported mass transfer experiments in which a cylindrical wetted wall column was used. They concluded that $\varepsilon_m / \varepsilon_v$ is less than 0.85. Their ideas about ε_m and ε_v differ from those of Rothfus and co-workers (16), Page and co-workers (34), Sherwood and Woertz (33), Hinze (68), and others. Schwarz and Hoelscher state that ". . . the diffusivity must tend toward infinity at the center line." However, in the derivations appended to their paper, they show that ε_v is the quotient of two quantities that vanish at $r = 0$. They do not show in their paper or appended derivations that this quotient increases without bound as r approaches zero.

Dhanak (35) conducted experiments similar to those of Sherwood and Woertz, but used different and more elaborate apparatus. He calculated "average" values of ε_m and ε_v and found the ratio, $\varepsilon_m / \varepsilon_v$, to be about 1.8.

Flint, Kada, and Hanratty (38) reported eddy diffusivities of mass calculated from tracer experiments. Small diameter injector tubes were centered in large pipes so as to approximate point sources in these experiments. Tracers of hydrogen and carbon dioxide were used when air was the main fluid and a concentrated, aqueous potassium chloride solution was used as a tracer when water was the main fluid. Eddy diffusivities were computed from concentration profiles at cross

sections downstream from the injection point. The value of the dimensionless quantity, $\varepsilon_m / 2r_w u_{max}$, was found to be 1.4×10^{-3} at a Reynolds number of 10,000 and to approach a limiting value of 8.2×10^{-4} at Reynolds numbers greater than 100,000.

Baldwin and Walsh (37) reported eddy diffusivities of heat calculated from temperature distributions downstream from a line source in a large pipe. The values of $\varepsilon_H / 2r_w u_{max}$ found at large Reynolds numbers approached a limiting value of 1.1×10^{-3}.

Hawthorn (69) extended the analysis of Tichacek, Barkelew, and Baron (58) for effective axial diffusivities to non-isothermal conditions. He assumed that $\varepsilon_H / \varepsilon_v = 1.0$ and divided the cross section of a pipe into three regions for the calculation of eddy diffusivities,

$$\frac{\varepsilon_v}{\nu} = n_D^2 u^+ y^+ [1 - \exp(-n_D^2 u^+ y^+)], \quad 0 \leq y^+ < 26 \qquad (25a)$$

$$\frac{\varepsilon_v}{\nu} = 2 N_H y^+_{max} \frac{r}{r_w} \left(A_H - \frac{r}{r_w}\right), \quad 26 \leq y^+ < 0.7\, y^+_{max} \qquad (25b)$$

$$\frac{\varepsilon_v}{\nu} = 0.6 N_H y^+_{max} \left(A_H - \sqrt{0.3}\right), \quad 0.7\, y^+_{max} \leq y^+ \leq y^+_{max} \qquad (25c)$$

where n_D, N_H, and A_H are empirical constants. Howthorn assumed a parabolic temperature distribution to obtain viscosity, μ, as a function of y^+ for $y^+ < 26$. Then he integrated an expression for du^+ / dy^+ containing $\mu(y^+)$ to obtain u^+ as a function y^+ for equation 25a. The effect of molecular viscosity is neglected for $y^+ > 26$.

Beek and Miller (70) presented a paper entitled "Turbulent Transport in Chemical Reactors." They gave qualitative discussions of several situations in which turbulent transport phenomena take part.

Irving and Smith (71) reported a recent analytical investigation of heat transfer to a reacting gas in turbulent pipe flow. Only the reversible decomposition of nitrogen tetroxide to nitrogen dioxide was considered. This reaction is so fast that the composition of the reaction mixture at any given point in the reactor was considered to be approximately equal to the equilibrium composition at the temperature and pressure existing at this point.

There is a clear distinction between the work of Irving and Smith and this investigation. They were interested in a heat transfer problem, complicated by a chemical reaction. In contrast, this investigation is directed towards chemical reaction problems that include heat transfer, among other complications.

Irving and Smith used the approach of Deissler (44) for heat transfer to fluids having variable fluid properties and assumed that $\varepsilon_H / \varepsilon_v = 1$. They found that the ratio of heat transfer coefficients for a reacting mixture and a "frozen" mixture might be as great as 9, depending on the bulk temperatures. They note that values ranging from 6 to 8 and as high as 12 were found in two experimental studies. In view of the density difference between mixtures rich in nitrogen dioxide and those rich in nitrogen tetroxide, one would expect to find a radial component of the temporal-mean velocity corresponding to the production of nitrogen dioxide in the vicinity of the pipe wall. It is remarkable

that the analysis of Irving and Smith agrees so well with experiment without taking into consideration a radial component of velocity.

Modelling Theory

Experiments with models are used in the fields of flow phenomena and heat transfer to establish formulas for predicting results in large-scale equipment. The success of this procedure in these fields suggests its application to the field of chemical reaction engineering. However, this approach has not been particularly fruitful. The following discussion of several representative contributions shows the progress made and some of the difficulties encountered.

Damkoehler (1) recognized in 1936 the possibility of using modelling theory as a basis for the prediction of the behavior of chemical reactions in large-scale equipment. He wrote the differential equations expressing the conservation of momentum, energy, and mass of a molecular species. From these, he deduced five characteristic dimensionless parameters as criteria of chemical similarity. These are

$$\frac{\rho u \ell}{\mu} = N_{Re}, \quad \frac{U' \ell}{\mu} = N_{D\ I}, \quad \frac{U' \ell^2}{D_m} = N_{D\ II}$$

$$\frac{H_R U\ \ell}{Z\rho\theta_D u} = N_{D\ III}, \quad \frac{H_R U\ \ell^2}{k_T \theta_D} = N_{D\ IV} \tag{26}$$

where U = reaction rate [equivalents/$(cm.^3)(sec.)$],

U' = $\nu_j U / C_j$ [$(sec.)^{-1}$]. The ν_j and C_j are stoichiometric coefficients and concentrations, respectively,

ℓ = a characteristic linear dimension [cm.],

H_R = heat effect of reaction [cal./ equivalent],

θ_D = *excess temperature, referred to an arbitrary* zero, [°C],

k_T = thermal conductivity [cal./ (cm.)(sec.)(°C)],

and D_m = molecular diffusivity [(cm.)^2/sec.].

Damkoehler first considered the case of complete similarity, that is, geometrical similarity and equality of the parameters, N_{Re}, $N_{D\ I}$, ..., $N_{D\ IV}$, for the same reaction in reactors of different scales.

Consider a change in the scale of the throughput, a quantity which is proportional to $\ell^2 u$. Let $\ell_2^2 u_2 = X\ell_1^2 u_1$ where X is the scaling constant. Damkoehler found that the equality of the similarity criteria requires that

$$\ell_2 = X\ell_1, \quad u_2 = X^{-1}u_1, \quad \theta_{D2} = \theta_{D1}, \text{ and } U_2 = X^{-2}U_1 \quad (27)$$

For simple reactions U can be regulated by means of the absolute temperature and complete similarity can be obtained. But, as he notes, similarity obtained in this way is economically impractical.

Damkoehler also considered the class of homogeneous reactions in tubular reactors where $N_{D\ II}$ is negligible and geometric similarity is abandoned. The results were essentially the same as those for the case of complete similarity. Specifically, he found that for a throughput scaling factor of X

$$u_2 = X^{-1}u_1, \quad d_2 = Xd_1, \quad L_2 = XL_1, \quad \theta_{D_2} = \theta_{D1} \text{ and } U_2 = X^{-2}U_1 \quad (28)$$

where d and L are tube diameter and length, respectively. He noted that an economically practical situation is obtained if the conditions for both geometrical and flow similarity are relaxed and $N_{D\,II}$ is neglected. In this case, the criteria of similarity are

$$\frac{U'L}{u} = N_{D\,I}, \quad \frac{U\,H_R L}{Z\rho\theta_D u} = N_{D\,III}, \text{ and } \frac{U\,H_R d^2}{\theta_D k_T N_{Nu}} = N_{D\,IV}/N_{Nu} \tag{29}$$

where N_{Nu} is the Nusselt criterion. Again assuming that the reaction is the same for both scales, Damkoehler showed that

$$a_2 = X^{0.286}\, a_1, \quad L_2 = X^{0.428}\, L_1, \text{ and } u_2 = X^{0.428}\, u_1 \tag{30}$$

Hulburt (72), in 1944, considered the problem of a homogeneous reaction in a tubular reactor. For the simple case where the sum of the stoichiometric coefficients (see equation 1) is zero and the reaction is first order, he wrote

$$\frac{d^2\gamma}{dz^2} - \frac{1}{\lambda_H}\frac{d\gamma}{dz} - \frac{N_{D\,I}\gamma}{\lambda_H} = 0$$

$$\gamma(0) = 1, \quad \frac{d\gamma(1)}{dz} = 0 \tag{31}$$

where γ is the fraction unconverted of a reference component and $\lambda_H = D/\bar{u}L$. The reader should note that the boundary conditions imposed by Hulburt were not discussed adequately. The correct treatment of the boundary conditions for axial diffusion models of tubular reactors was given later by Wehner and Wilhelm (73).

Hulburt's solution to system 31 contained the product $\lambda_H N_{DI}$ as a parameter. He claimed that the effect of diffusion would rarely be important since the maximum value of $\lambda_H N_{DI}$ found in practice is small, on the order of 10^{-2}. This argument was based on the orders of magnitude of molecular and turbulent diffusion coefficients for gases and liquids. The argument would be correct if mixing in tubular reactors occurred solely by diffusion in the direction of flow. However, from the work of Bosworth (53, 54), Taylor (56, 57), Tichacek, Barkelew, and Baron (58), and the experimental results quoted in these papers, it is known that the mixing caused by the interaction between radial diffusion and a radial variation in velocity is large compared to true axially-directed diffusion. If Hulburt's values of diffusivity, D, are replaced by Taylor's virtual axial diffusivities, D_T, the value of $\lambda_H N_{DI}$ which Hulburt calculated to be 0.01 would be on the order of 50 for liquids in turbulent flow and 500 for gases in turbulent flow. For laminar flow, if inequality 21 were satisfied, the value of $\lambda_H N_{DI}$ would be on the order of 10^4 for liquids and 10^8 for gases.

D'yakonov (74) criticizes Damkoehler severely for omitting consideration of the criterion of chemical equilibrium from the conditions of chemical similarity. Thus, if a process as a whole is never far from equilibrium, the problem may be treated from a purely thermodynamic viewpoint. Besides this case, D'yakonov states that approximate similarity may be attained if the chemical reaction is non-equilibrium but the transport processes for mass, heat, and momentum are in

equilibrium, or if the reaction is in equilibrium and the transport processes are not. He does not seem to consider at all the important case where neither reaction nor transport are equilibrium processes.

Johnstone and Thring (75) wrote a most comprehensive and practical book on the theory and applications of modelling. They added Thring's radiation criteria to the five similarity criteria obtained by Damkoehler and arrived at

$$N_{DI} = \frac{\nu_j UL}{C_j \bar{u}} = \psi(N_{Sc}, N_{Pr}, N_{Re}, \frac{H_R C_j}{Z\rho T}, \frac{\rho Z \bar{u}}{\sigma e T^3}, \frac{T}{T_r}) \qquad (32)$$

where T = absolute temperature of the reaction mixture,

σ = Stefan-Boltzmann constant,

e = combined emissivities of radiating and absorbing surfaces,

T_r = absolute temperature of corresponding points on radiating surfaces,

and Z = heat capacity.

Johnstone and Thring state that "This is the generalized rate equation for a continuous-flow, chemically-reacting system. Certain minor effects such as heat transfer by natural convection have already been neglected, but equation 32 still contains seven dimensionless groups which cannot all be kept constant when the size of the system is changed. Certain of these groups can be in practice neglected without seriously affecting similarity, but this may introduce an appreciable scale effect, a possibility which has to be borne in mind when a chemical reaction is scaled up or down." For homogeneous reactions in geometrically similar vessels they suggest that 32 may be simplified to

$$N_{DI} = \psi\left(\frac{H_R C_j}{Z \rho T}, \frac{H_R C_j u}{Q_w}\right) \tag{33}$$

where Q_w is the heat flux density at the reactor wall. Thus, for a scale-up ratio of X, they obtain

$$L_2 = XL_1, \qquad Q_{w2} = XQ_{w1}, \qquad v_2 = X^3 v_1, \qquad J_2 = X^3 J_1 \tag{34}$$

where v is the volumetric flow rate and J is the total heat loss per unit time through the reactor walls. Finally, they mention that for gas phase reactions in tubular reactors it is necessary to have the same pressure drop across both the model and the prototype reactor unless the pressure drop is negligible compared to the absolute pressure at the reactor inlets.

Fan and Bailie (76) formulated a piston-flow, axial-diffusion model for tubular reactors and isothermal reactions of arbitrary order. They wrote

$$\frac{d^2\gamma}{dz^2} - 2 N_{Pe} \frac{d\gamma}{dz} - N_{Pe} N_{DI} \gamma^n = 0$$

$$z = 0, \qquad \frac{d\gamma}{dz} = 2 N_{Pe}(\gamma_{o+} - 1) \tag{35}$$

$$z = 1, \qquad \frac{d\gamma}{dz} = 0$$

where $N_{Pe} = \bar{u}L / 2D_I$ (a modified Peclet number), n is the order of the reaction, $z = x/L$, the relative displacement from the reactor inlet, and γ is the unconverted fraction of the feed concentration,

that is, $\gamma = 1$ for $z < 0$. This formulation implies chemical similarity in two reactors of different scales if the values of N_{Pe} and of N_{DI} are equal and if the reaction orders are the same.

Models of Tubular Reactors

The behavior of reactions in tubular reactors has been described by five kinds of mathematical models. In this study, these models are designated by the names: autoclave-series, piston-flow, distributed-velocity, axial-diffusion, and radial-diffusion models. In the following treatment the discussions of previous contributions are grouped according to the kind of model used. Work that specifically concerns heterogeneous reactions is not included unless it also is helpful in the solution of the problem for homogeneous reactions in chemical reactors. Contributions dealing with the special problem of programmed control and interaction between thermal and chemical phenomena are considered separately from the general contributions concerning tubular reactors.

Autoclave-Series Models.--The use of an autoclave-series model of a tubular reactor permits the use of the algebraic and graphical methods described by Eldridge and Piret (77), Schoenemann (78) and others. In many instances, these methods permit calculations for an autoclave-series model to be made more readily than analogous calculations using any other type of model.

The studies of residence-time distributions made by Danckwerts (55) and by Kramers and Aberda (59) indicate that the residence-time distribution for turbulent flow in pipes may be approximated by the

residence-time distribution of flow through a series of properly-sized, perfect mixers. The mathematics of reactions proceeding in a series of perfect mixers involves only algebraic equations so that the mathematical complications of differential equations and partial differential equations may be avoided. Under the circumstances, it is natural to consider the mathematics of the perfectly-mixed autoclave series as a model of a tubular reactor for which the flow is turbulent. The autoclave-series models have another important advantage in that the effects of heat transfer, density changes, and competing reactions can be handled more simply than with any other kind of model of a tubular reactor. For these reasons, it is appropriate to review some of the more important contributions to the theory of an autoclave series.

An early development in the theory of chemical reactions in an autoclave series was made by MacMullin and Weber (79) in 1935. They developed equations for the conversions of uni-directional, homogeneous reactions of first, second, and third order in a series consisting of an arbitrary number of vessels.

Denbigh (4) discussed the comparative output per unit volume of reaction space in batch and continuous-flow, stirred autoclaves. He pointed out that, for all reactions of orders greater than unity, the greatest overall productivity for a given total volume of an autoclave series is obtained if the volumes of the autoclaves increase in the direction of flow. Denbigh also considered the comparative yields of useful product obtainable by batch and continuous operation in the case of competing reactions. He showed that this yield is controllable

to some extent by the choice of a batch or continuous system and, within a continuous system, by the ratio of the volumes of the consecutive autoclaves in the series.

Eldridge and Piret (77) summarized earlier work on the theory of an autoclave series and tabulated design equations for uni-directional, reversible, simultaneous, and consecutive reactions of various orders. They presented experimental data for the hydrolysis of acetic anhydride in a five-member series of 1.8-liter, stirred autoclaves. These data agreed extremely well with the theoretical predictions obtained from their design equations.

Schoenemann (78) presented some design equations for an autoclave series and discussed some examples from industrial practice. He showed a method that may be used for the graphical determination of the chemical conversion in a continuous-flow reactor when the form of the rate equation is unknown. This method requires an experimental determination of conversion as a function of holding time in a laboratory-size, batch reactor plus an experimental residence-time distribution for the large-scale reactor.

Horn and Kuechler (80) pointed out that the method of Schoenemann, mentioned in the preceding paragraph, is strictly applicable either if the reaction is first order or if the reaction mixture is divided into a large number of very small (compared to vessel size), discrete, but homogeneous, parts between which there is no mass transfer. For cases where these conditions do not hold, Horn and Keuchler presented a diagram for estimating the size of the error in Schoenemann's method.

Broetz (81) made extensive use of the theory of continuous-flow autoclaves and autoclave series in his book on chemical reactor technology. All of the work mentioned above on autoclave series, except that of Denbigh, has been entirely concerned with isothermal reactions. Broetz extended the theory to consider adiabatic and non-adiabatic reactors, exothermic and endothermic reactions, and reaction mixtures having variable density.

Piston-Flow Models.--Piston-flow models of a tubular reactor have been very popular because of their conceptual simplicity. The main features of this type of model are a uniform velocity throughout a reactor cross section, perfect mixing of the reacting fluid in the radial direction and no mixing in the axial direction.

The main distinction between this type of model for a tubular reactor and the autoclave-series type is that in this case the equations relating the conversion and temperature to reactor length are differential equations instead of algebraic equations. In a great many cases of practical importance, analytical solutions to these differential equations cannot be obtained readily. Hence the mathematics of this type of model may be more complex than the mathematics of the autoclave-series type.

Hougen and Watson (82) and Smith(83) presented a stepwise method for the solution of reactor design problems using a piston-flow model. This method is really a rudimentary form of numerical integration of the basic differential equations. Walas (84) formulated a method specifically in terms of numerical integration and used a numerical

formula that is more accurate than that of Hougen and Watson, but which is still elementary. The authors mentioned in this paragraph consider cases where the reaction is kinetically complex, fluid properties are not constant, the heat effect of the reaction is not negligible, and there is heat exchange between the reaction mixture and the wall of the reactor.

Murdoch and Holland (85) described a shortcut calculation method for first-order, endothermic reactions in fired tubular reactors. They divided the reactor into sections and wrote ordinary differential equations relating temperature, conversion of a key reactant, and pressure drop to the displacement from the inlet of a reactor section. In their model, the first section of the reactor serves as a preheater and the length of this section is adjusted to give a conversion of 0.01 at its outlet. Simplifying approximations were made which permitted approximate solutions to the basic differential equations to be obtained analytically. For example, the temperature dependent part of the rate coefficient has the form e^{aT} instead of the usual $e^{-a/T}$. The properties of the reaction mixture and the rate of heat input were assumed to be constant within a reactor section. In addition, this method is limited to reactions for which the heat of reaction does not vary greatly with conversion.

Perkins and Rase (86) attacked essentially the same problem as Murdoch and Holland. However, they integrated the differential equations numerically using an explicit formula due to Adams (87). The use of this formula permitted them to apply their method even in cases where the heat of reaction and rate of heat input vary considerably.

Perkins and Rase pointed out that the use of Adams' formula eliminates the need for solutions by trial in the stepwise calculations for successive reactor sections.

Billingsley, McLaughlin, Welch, and Holland (88) reported a method for the design of flow- or batch-type tubular reactors heated by condensing vapors. This method applicable to first-order and pseudo-first-order, endothermic, liquid-phase reactions. These authors wrote the differential equations relating conversion and temperature of the reaction mixture to the displacement from the reactor inlet. Several hundred numerical solutions were obtained for these equations, and the solutions were correlated and presented in the form of nomograms. Constant properties of the reaction mixture, a constant heat transfer coefficient and a constant wall temperature, were assumed in this analysis.

Bilous and Amundson (89) investigated the stability and sensitivity of several classes of chemical reactors. They used a piston-flow model to describe the steady state for a tubular reactor and pointed out that even this simple model serves to illustrate the complexities that can occur in the design and operation of reactors.

Gee, Linton, Maier, and Raines (90) reported an investigation of a non-catalytic, homogeneous, gas-phase reaction that takes place in a non-adiabatic, non-isothermal, jacketed, tubular reactor. In this reaction, two reactants were preheated independently before their introduction into the reactor. The jacket of the reactor was divided into three independent sections. Temperature control of the reaction mixture was effected by heat transfer between the reaction mixture

and fluid streams circulating through the three jackets. In the particular reaction considered by these authors, the products of degradation of components of the reaction mixture formed a coke-like, insulating layer on the inside of the reactor wall. Naturally, the growth of such a layer interfered with heat transfer from the reaction mixture and prevented adequate temperature control.

Gee and co-workers wrote three simultaneous, ordinary differential equations to relate conversion, temperature, and pressure drop to displacement from the reactor inlet. A fourth differential equation expressed the fouling of the heat transfer surface as a function of temperature, time, and flow rate. In addition to the usual assumptions of a piston-flow model, these authors assumed that the reaction mixture could be described by the perfect gas laws, an average molecular weight, an average heat capacity, and an average heat of reaction. Gee and co-workers solved their system of differential equations by numerical integration. The computed results were correlated with plant experience and were used to predict improved conditions for plant operation.

Distributed-Velocity Models.--A model of a tubular reactor which takes into account the radial variation of the temporal-mean velocity, but neglects both radially-directed and axially-directed diffusion, will be called a distributed-velocity model. This type of model should provide an accurate description of tubular reactor operation provided that the temperature of the reaction mixture is essentially uniform, an accurate residence-time distribution is used, and the reaction is first order. As Danckwerts (91) shows, this type of model is not

rigorously correct for other than first-order reactions unless mixing and diffusion are negligible. Thus, this type of model is accurate for non-first-order, liquid-phase, reactions in laminar flow, only if Bosworth's criteria, inequalities 18 and 19, are satisfied.

Denbigh (92) used a distributed velocity model for a second-order reaction under conditions of laminar flow, constant temperature and constant fluid properties. He combined an expression for the residence-time distribution of laminar flow with the integrated relation between conversion and residence time and obtained for the average conversion at the reactor outlet

$$\overline{W} = \frac{C^{o}k_{R}L}{\overline{u}}\left[1 + \frac{(C^{o}k_{R}L/2\overline{u})\ \ln(C^{o}k_{R}L/2\overline{u})}{1 + (C^{o}k_{R}L/2\overline{u}}\right] \qquad (36)$$

where $\overline{W}$ = is the bulk-average conversion at the reactor outlet,

C^{o} = is the inlet concentration,

and k_{R} = is the second-order reaction rate coefficient.

Use is made of a distributed-velocity model by Roughton and Millikan (93) and Dalziel (94) in the field of fast-reaction kinetics. The mean conversion, $\overline{W}$, is obtained from

$$\overline{W} = \frac{1}{A_{t}}\int_{o}^{A_{t}} W(\frac{L}{u})\ da \qquad (37)$$

where $W(t)$ is the batch conversion,

L is the tube length,

u is the temporal-mean velocity, a function of radius,

and A_{t} is the tube cross sectional area.

The velocity, u, is computed from the Poiseuille equation for laminar flow or from "Prandtl's equation,"

$$u = 1.225\ \bar{u}(y/r_w)^{1/7}$$

for turbulent flow. These investigators present tables of the difference between the "true" average conversion, obtained from equation 37, and the apparent conversion, $\bar{W} = W(L/\bar{u})$.

Axial-Diffusion Models.--Axial-diffusion models for a tubular reactor are related to the piston-flow type of model. A uniform velocity throughout a reactor cross section and perfect mixing of the reacting fluid in the radial direction are assumed as before. However, axial diffusion is no longer neglected. Taylor (57) showed that the combined effects of a radial variation in the axial component of velocity and radial diffusion were equivalent to a virtual axial diffusion of the bulk-average concentration and temperature. One must remember that this apparent diffusion is the result of these combined effects, and is not true diffusion in the axial direction, which is usually negligible by comparison.

So far, the only published treatment of non-isothermal reactions using an axial-diffusion model is that of van Heerden (95). He discussed the character of the steady state of exothermic reactions. In view of Hawthorn's (69) treatment of axial mixing in the presence of radial temperature variation, further investigations of non-isothermal conditions should be possible using this model of a tubular reactor.

The additional mathematical complications encountered in the axial-diffusion type of model are mainly connected with boundary

conditions. A differential equation relating conversion to the displacement from the reactor inlet is a first-order equation for the piston-flow type of model, so only one boundary condition is needed. However, the analogous equation for an axial-diffusion model is a second-order ordinary differential equation, requiring two boundary conditions. This might seem a trivial complication, but one should remember that the conversion in either the feed or the effluent stream must be treated as an unknown and that, generally speaking, there is no a priori knowledge of the derivative of conversion with respect to displacement anywhere within the reactor.

Hulburt (72) proposed an axial-diffusion model of a tubular reactor. However, he was not aware of the size of the coefficient for virtual axial diffusion and considered the effect of the diffusion term in his model to be negligible. This work was discussed in the section on Modelling Theory, above.

Danckwerts (55) considered an axial diffusion model for a first-order reaction and obtained an analytical solution for this case. He obtained boundary conditions for the inlet and outlet of the reactor from consideration of material balances for a reactant.

Wehner and Wilhelm (73) discussed in some detail the boundary conditions for axial-diffusion models of a tubular reactor. They showed that the conditions used by Danckwerts are a special case of more general conditions.

Suppose a reaction begins abruptly at the reactor inlet, $z = 0$, and terminates abruptly at the outlet, $z = 1$. This might occur if the

reactor contained a fixed bed of catalyst for a heterogeneous reaction. For homogeneous reactions, the abrupt beginning of the reaction at $z = 0$ could correspond to the mixing of reactants or a homogeneous catalyst at this point. Such an abrupt beginning and termination might also be approximated in photolytic reactions. The general equations presented by Wehner and Wilhelm are

$$D_{T1} \frac{d^2\gamma}{dz^2} - L \bar{u}_1 \frac{d\gamma}{dz} = 0, \qquad z < 0 \tag{38a}$$

$$\frac{d^2\gamma}{dz^2} - \frac{L\bar{u}_2}{D_{T2}} \frac{d\gamma}{dz} - \frac{L^2 k_R c_f^{n-1} U_c(\gamma)}{D_{T2}} = 0, \qquad 0 \leq z \leq 1 \tag{38b}$$

$$D_{T3} \frac{d^2\gamma}{dz^2} - L \bar{u}_3 \frac{d\gamma}{dz} = 0, \qquad z > 1 \tag{38c}$$

$$\gamma \to 1 \quad \text{as} \quad z \to -\infty \tag{39a}$$

$$\gamma \to \Gamma \quad \text{as} \quad z \to \infty \tag{39b}$$

$$- D_{T1}\left(\frac{d\gamma}{dz}\right)_{0^-} + L \bar{u}_1 \gamma_{0^-} = - D_{T2}\left(\frac{d\gamma}{dz}\right)_{0^+} + L \bar{u}_2 \gamma_{0^+} \tag{39c}$$

$$- D_{T2}\left(\frac{d\gamma}{dz}\right)_{1^-} + L \bar{u}_2 \gamma_{1^-} = - D_{T3}\left(\frac{d\gamma}{dz}\right)_{1^+} + L \bar{u}_3 \gamma_{1^+} \tag{39d}$$

where the subscript notations f_{a^+} and f_{a^-} are abbreviations for the right-hand and left-hand limits, respectively, of f at $z = a$, and where

$\gamma = C/C_f$, the ratio of concentration C at displacement x to the feed concentration, C_f,

z = x/L, ratio of displacement from reactor inlet, x, to reactor length, L,

D_T = Taylor's virtual axial diffusivity,

and $U_c(\gamma)$ = Concentration-dependent part of reaction rate expression.

In this formulation, the reactor is considered together with an inlet and an outlet section. In the inlet section, the reaction mixture has a bulk velocity, $\bar{u}$, a virtual diffusivity D_{T1} and there is no reaction. This is expressed by equation 38a. In the reactor, the velocity and diffusivity are $\bar{u}_2$ and D_{T2}, which are not necessarily equal to the corresponding quantities for the inlet section. The differential equation describing the reactor is 38b. Equation 38c describes the outlet section where the velocity is $\bar{u}_3$ and the diffusivity is D_{T3}. The boundary conditions for these three differential equations are given by 39. The first two of these four express the constancy of γ far upstream and downstream from the reactor and the last two express the conservation of mass at the reactor inlet and outlet. The boundary conditions of Danckwerts,

$$\gamma_{o^+} = 1 + \frac{D_T}{L\,\bar{u}_2}\left(\frac{d\gamma}{dz}\right)_{o^+} \quad \text{at} \quad z = 0 \tag{40a}$$

and

$$\left(\frac{d\gamma}{dz}\right)_{1^-} = 0 \quad \text{at} \quad z = 1 \tag{40b}$$

can be obtained by letting $D_{T1} = 0$ and $D_{T3} = 0$. Then, from 38a and 39a $\left(\frac{d\gamma}{dz}\right)_{o^-} = 0$, and $\gamma_{o^-} = 1$. From 39c

$$\gamma_{0+} = \frac{\bar{u}_1}{\bar{u}_2} + \frac{D_I}{L\,\bar{u}_2}\left(\frac{d\gamma}{dz}\right)_{0+} \tag{40b}$$

which is the same as the first equation of 40a if $\bar{u}_1 = \bar{u}_2$. Note that since $\left(\frac{d\gamma}{dz}\right)_{0+}$ is negative, $\gamma_{0+} < \gamma_{0-}$. From 38c and 39b $\left(\frac{d\gamma}{dz}\right)_{1+}$ and $\gamma = \Gamma$ and from 39d

$$\gamma_{1-} = \frac{\bar{u}_3}{\bar{u}_2}\Gamma + \frac{D_I}{L\,\bar{u}_2}\left(\frac{d\gamma}{dz}\right)_{1-} \tag{40c}$$

Danckwerts reasoned that if $\left(\frac{d\gamma}{dz}\right)_{1-}$ were negative, the concentration in the outlet section would be greater than at the end of the reactor. If $\left(\frac{d\gamma}{dz}\right)_{1-}$ were positive, the concentration would pass through a minimum somewhere in the reactor and then rise toward the downstream end. He wrote, "Intuition suggests that neither of these conditions can arise so that the boundary condition must be $dc/dy = 0$ at $y = L$ [$d\gamma/dz = 0$ at $z = 1$ in the present notation]." The choice, $\left(\frac{d\gamma}{dz}\right)_{1-} < 0$, would seem to be as defensible as the choice, $\left(\frac{d\gamma}{dz}\right)_{1+} < 0$, at the reactor inlet. However, if these conditions are chosen simultaneously, the problem does not seem to have a unique solution unless 39a or 39b are used.

Hulburt's condition, $\gamma_{0+} = 1$, can be obtained from equation 40a if $\left(\frac{d\gamma}{dz}\right)_{0+} = 0$. However, this latter condition would contradict the presence of a reaction inside the reactor.

For homogeneous reactions initiated by heating, the problems with boundary conditions are easily avoided. For example, obvious choices for equation 38b and the analogous energy equation are

$\gamma = 1$, $d\gamma/dz = 0$, $T = T_0$, $dT/dz = 0$ at $z = 0$.

Levenspiel and Bischoff (96) solved equation 38b with Danckwerts' boundary conditions, 40a. They presented graphs of solutions for first and second order reactions. Fan and Bailie (76) also solved equation 38b with Danckwerts' boundary conditions. They obtained numerical solutions for reaction orders of 1/4, 1/2, 2, and 3 and displayed graphs of these solutions for a number of combinations of $(L\,\bar{u})/D_T$ and $(L^2 k_R C_f^{n-1})/D_T$.

Tichacek (97) used an axial-diffusion model for part of his paper on selectivity in experimental reactors. His definition of selectivity is closely related to chemical efficiency, as defined in this thesis, but they are not identical. He obtained an analytical solution for a system of three first order reactions. Instead of Danckwerts' condition, $d\gamma/dz = 0$ at $z = 1$, Tichacek used $\gamma \to 0$ as $z \to \infty$. For initial conditions, he used

$$\gamma_{Ao+} = 1 + \frac{D_T}{L\bar{u}} \left(\frac{d\gamma_A}{dz}\right)_{o+} \tag{41a}$$

if $\gamma_{Ao-} = 1$, and

$$\gamma_{Ao+} = \frac{D_T}{L\bar{u}} \left(\frac{d\gamma_A}{dz}\right)_{o+} \tag{41b}$$

if $\gamma_{Ao-} = 0$.

Tichacek defined δ^T, the loss in selectivity due to axial mixing, as the difference between the maximum amount of desired product with and without axial mixing, divided by the maximum amount which could be produced without axial mixing. He then showed that in several important cases

$$\delta_j^T \doteq D_T / L_j^* \bar{u} \qquad (42)$$

for small $D_T / \ell_j^* \bar{u}$, where ℓ^* is a characteristic axial displacement and the subscript refers to the j^{th} product. The approximation, 42, is used to design experimental reactors that minimize axial mixing due to Taylor's virtual diffusion. Such reactors can be used for accurate determination of rate coefficients and for predicting chemical efficiencies and conversions in ". . . a properly designed plant-scale reactor." Tichacek's analysis is limited to isothermal reactions and to straight tubular reactors, that is, without bends or coils.

Radial-Diffusion Models.--A radial-diffusion model of a tubular reactor may be considered as a more complicated version of a distributed-velocity model. In this type, the temporal-mean velocity varies with radius and radial diffusion is taken into account, but axial diffusion is neglected. The coefficient of radial diffusion has a finite value, so that radial mixing is not perfect, as it is in piston-flow and axial-diffusion models.

None of the five types of mathematical models considered in this chapter gives a true and complete description of the physical and chemical phenomena that occur in a tubular reactor. Each of the types represents a compromise between the demands of accurate description and those of mathematical simplicity. Radial-diffusion models give a more detailed picture of the phenomena than models of the other four types, so they are capable of giving greater accuracy. However, the cost of this more detailed picture is the replacement of ordinary differential equations by partial differential equations and the replacement of lumped parameters by distributed parameters.

The comparative advantages and disadvantages of radial-diffusion and axial-diffusion models are worth mentioning. First of all, to the extent that the radial transport of heat and mass is less than perfect, the description furnished by the radial-diffusion type of model is superior to that of the axial-diffusion type. The fact that resistances to radially directed heat and mass transport are not zero gives rise to distributions of temperature and concentrations in the reaction mixture and, thereby, to a distribution of reaction rate. The possibility of guaranteeing that the temperature and concentration obtained from an axial-diffusion model will give a reaction rate that approximates the average reaction rate at a reactor cross section seems very remote because of the non-linear nature of the distributions.

Mathematically, radial-diffusion models are certainly more complicated than axial-diffusion models. The former lead to boundary value problems that include partial differential equations, whereas the latter involve only ordinary differential equations. Neither of these types of models yield boundary value problems that can be solved analytically except in special cases. Of the two, the amount of computation required to obtain an approximate solution is greater for the radial-diffusion type. On the other hand, the boundary conditions in radial-diffusion models do not have a tendency to confound intuition. Furthermore, the simplicity of the lumped velocity and diffusion parameters in the axial-diffusion models is only an apparent simplicity. In these, the calculation of D_T requires an accurate knowledge of the velocity and diffusivity distributions, just as in the radial-diffusion models.

Cleland and Wilhelm (98) proposed a radial-diffusion model for a first-order reaction in a tubular reactor under conditions of constant temperature and laminar flow. From the conservation of mass for a reactant, they derived the relation,

$$\frac{D_m}{k_R r_w^2}\left[\frac{\partial^2 \gamma}{\partial s^2} + \frac{1}{s}\frac{\partial \gamma}{\partial s}\right] - \frac{u_{max}}{k_R}(1 - s^2)\frac{\partial \gamma}{\partial x} - \gamma = 0 \qquad (43)$$

where $s = r/r_w$,

γ = fraction of feed concentration unconverted,

and k_R = first-order reaction-rate coefficient.

The boundary conditions are

$$\gamma = 1 \quad \text{at} \quad z = 0, \qquad \frac{\partial \gamma}{\partial s} = 0 \quad \text{at} \quad s = 1 \qquad (44a)$$

and because of symmetry about the axis

$$\frac{\partial \gamma}{\partial s} = 0 \quad \text{at} \quad s = 0 \qquad (44b)$$

As an analytical solution to this boundary value problem for the special case where $D_m/(k_R r_w^2) = 0$, Cleland and Wilhelm obtained

$$\bar{\gamma}(\lambda_c) = \frac{2}{\bar{u}}\int_0^1 u\gamma s\, ds = e^{-\lambda_c}(1 - \lambda_c) + \lambda_c^2 \int_\lambda^\infty \frac{e^{-p_c}}{p_c}\, dp_c \qquad (45)$$

where $\lambda_c = k_R x / u_{max}$

$p = \lambda_c/(1 - s^2)$

For a hypothetical case where $D_m/(k_R r_w^2)$ becomes large without limit, Cleland and Wilhelm stated that ". . . the radial concentration gradients must necessarily vanish. The situation is now as though the reaction were occurring in 'plug' flow. For this case the concentration of reactant leaving the reactor is given by $C = e^{-2\lambda_c}$ [$\gamma = e^{-2\lambda_c}$ in the present notation]." Cleland and Wilhelm solved the general boundary value problem given in 43 and 44 by the Crank-Nicolson (99) numerical method. Numerical solutions for the two special cases mentioned above were found to be in excellent agreement with the analytical solutions.

These investigators also reported the results of a parallel experimental investigation. The aqueous hydrolysis of acetic anhydride, a pseudo-first-order reaction, was used in this work. The ranges of the experimental variables were

Temperatures	25°C and 35°C
Tube diameter	1/4 in. and 1/2 in. I. D.
Tube length	10 ft. and 15 ft.
Velocity (maximum)	1.15 to 6.85 cm./sec.
Reynolds number	40.3 to 398
$k_R L/u_{max}$	0.287 to 1.84
$\bar{\gamma}$	0.04 to 0.71

The experimental values of $\bar{\gamma}$ at the reactor outlet and those predicted by the theoretical model were compared and agreed fairly well. The largest difference between them was about four per cent of the inlet values. The experimental values of $\bar{\gamma}$ for the 1/2-inch reactor tended to be smaller than those for the smaller reactor. This result was explained by natural convection effects.

Chambré (100) presented an analysis of chemical reactions in internal flow systems. He assumed constant properties of the reaction mixture, but permitted heat exchange between the reaction mixture and the vessel wall and heat generation or absorption by the reaction. At the end of his general development he wrote, "The solution to the complete problem is thus reduced to the rather difficult solution of either a non-linear integro-partial differential equation or to a non-linear partial differential equation. However, under the condition of small temperature changes to which the present analysis primarily applies one can obtain the solution quite easily." Chambré's next step was to write his partial differential equation for the extent of reaction in terms of a new variable, τ_c, the generalized isothermal reaction time. An approximate linear partial differential equation was then obtained by developing τ_c in a perturbation series. "Thus to this approximation the solution of the problem has been reduced to the solution of the two Sturm-Liouville systems [46, Chambré's equation 25] and [47, Chambré's equation 38]. These solutions are already known for both a constant and a laminar velocity profile. In the latter case, the solution to [46] was first considered by Graetz. Jacob has reviewed this problem [(101), Chambré's reference 6]. Equation [47] was investigated by Sparrow and Siegel [(102), Chambré's reference 4]." The systems referred to by Chambré are

$$\frac{1}{s}\frac{d}{ds}\left(s\frac{dy_n}{ds}\right) + \delta_n f_c(s)\, y_n = 0, \qquad n = 0, 1, \ldots \tag{46a}$$

$$y_n(1) = y_n'(0) = 0 \tag{46b}$$

$$B_n = \frac{\int_0^1 s\, f_c(s)\, y_n(s)\, ds}{\int_0^1 s\, f_c(s)\, y_n^2(s)\, ds} \tag{46c}$$

and

$$\frac{1}{s}\frac{d}{ds}\left(s\,\frac{dw_n}{ds}\right) + \lambda_n f_c(s)\, w_n = 0, \qquad n = 0, 1, \ldots \tag{47a}$$

$$w_n'(0) = w_n'(L) = 0 \tag{47b}$$

where $s = r/r_w$

and $f_c(s) = u(s)/2\bar{u}$

Chambré illustrated the general analysis by the case of a first-order reaction and a laminar velocity distribution where the fluid temperature at the reactor inlet is the same as the wall temperature. An approximate solution is obtained in the form

$$\xi_c(\zeta,s) = (1 - e^{-2\alpha\zeta}) + \alpha\, e^{-2\alpha\zeta} \sum_{m=0}^{\infty} (1 - e^{-\lambda_m\zeta})\,\frac{c_m w(s)}{\lambda_m} \tag{48}$$

$$\theta_c(\zeta,s) = \alpha\, e^{-2\alpha\zeta} \sum_{n=0}^{\infty} \left\{ \frac{2\,B_n}{\delta_n - 2\alpha}\, y_n(s) \left[1 - e^{-(\delta_n + 2\alpha)\zeta}\right] \right. \tag{49}$$

$$+ \sum_{q=0}^{n} \frac{B_s c_{n-q} w_{n-q}(1) y_q(s)}{\delta_q - \lambda_{n-q} - 2\alpha} \left[e^{-\lambda_{n-q}\zeta} - e^{-(\delta_q + 2\alpha)\zeta}\right]$$

$$\left. - \frac{c_n}{\lambda_n}\left[w_n(1) - w_n(s)\right]\left[1 - e^{-\lambda_n\zeta}\right] \right\}$$

where ξ_c is the extent of reaction,

$$\theta_c = \frac{Z(T - T_w)}{H_R} ,$$

$$\alpha = \frac{k_R r_w^2}{D\rho} ,$$

$$\zeta = \frac{xD}{2\bar{u}r_w^2} ,$$

and $$c_m = \int_0^1 s\, w_m(s)\, ds, \quad m = 0, 1, \ldots .$$

Chambré mentioned that his analysis may be extended to several simultaneous reactions and turbulent flow and indicated some of the essential steps in such an extension.

Chambré's equation 48 supports the belief of Cleland and Wilhelm that the solution to the differential equation for a radial-diffusion model approaches the solution to the differential equation for a piston-flow model as $D/k_R r_w^2$ become large. First of all, this is obviously true for $k_R \to 0$ as $D/k_R r_w^2 \to \infty$, so a constant $k_R \neq 0$ is considered. Now, write the product $\zeta\alpha$ as

$$\zeta\alpha = \frac{k_R x}{2\rho\bar{u}}$$

and let ρ and $\bar{u}$ be constants. Here, α is inversely proportional to $D/k_R r_w^2$ or D/r_w^2. Under the above conditions, $D/k_R r_w^2 \to \infty$ implies that $\alpha \to 0$ and $\zeta \to \infty$ for a constant displacement, x, from the inlet. When the constant quantity $k_R x/2\bar{u}\rho$ is substituted in equation 48, the result is obtained immediately since the second term on the right vanishes as $\alpha \to 0$.

The limitations on the application of the type of solution obtained by Chambré should be noted. First of all, it cannot apply rigorously to gas-phase reactions in which there is a significant density change because of the basic assumption of constant fluid properties and a fixed velocity distribution. Second, since the error of Chambré's perturbation series approximation is of the order of $k_R r_w^2/(D\rho)$, this type of solution will be poor for liquid-phase reactions unless $k_R r_w^2$ is very small, because of the smallness of D_m.

Some Special Problems of Exothermic Reactions.--One of the notable advances in chemical reaction engineering in the last decade is the theoretical approach to reactor design and control problems for exothermic reactions.

In 1953, van Heerden (103) defined an "autothermal process" as one in which the temperature level at which the reaction proceeds is maintained by the heat of reaction. He showed that there are ranges of temperatures and flow rates outside of which an autothermal process cannot exist. In a later and more complete publication, van Heerden (95) discusses autothermal processes in adiabatic, continuous-flow, well-mixed autoclaves (uniform concentration and temperature), tubular reactors (piston-flow) with heat exchange between inlet and outlet, and adiabatic tubular reactors with axial diffusion. He showed that in each of these cases where there is a "feedback of heat along the reaction path" two stable, steady-state conditions of the reaction mixture may exist for a given set of operating conditions. The temperature and conversion of one of these states are relatively low compared to those

of the other state. There is an ignition or hysteresis phenomenon associated with these autothermal processes. To change the type of steady state of the reaction mixture from small-conversion to large-conversion, the reaction mixture must receive a transient heat input to raise the temperature to that of the large-conversion steady state. Similarly, the reverse change requires a transient heat removal. Van Heerden's analysis permits the prediction of ranges of operating temperature and feed rate in which the behavior of a reaction will be autothermal.

Broetz (104) extended van Heerden's analysis for continuous-flow, stirred autoclaves to include the effect of heat transfer between the reaction mixture and a heat exchange fluid.

Bilous and Amundson (89) approached the phenomena of exothermic reactions from a different direction. While van Heerden was mainly interested in the description and means of attainment of autothermal conditions, Bilous and Amundson were interested in control problems. The equations of a piston-flow model of a tubular reactor yield only one steady state for a given set of parameters. However, they noticed that small changes in these parameters cause, under some conditions, large changes in conversions and temperatures. Bilous and Amundson termed this behavior "parametric sensitivity" and illustrated it by several specific examples. They presented a theoretical analysis of stability and control problems for a piston-flow model with and without the recycle of effluent. This analysis uses the methods of systems engineering to predict the response that results from sinusoidal or step-function variation in the initial temperature and concentration,

considered as input signals. In a later paper Coste, Aris, and Amundson (105) used a statistical approach to predict the response of a piston-flow model to random variations of input signals.

A discussion of other contributions along these lines was given by Foss (106) in a review of work on the dynamics of chemical reaction systems. This review is especially valuable because it includes the viewpoint of automatic control engineering and mentions some unsolved problems of importance.

Programmed Control and Optimization.--Another important advance in chemical reaction engineering is the prediction of optimal programs of control both for tubular reactors and autoclave series.

The importance of programmed control seems to have been recognized first by the Russians, Temkin and Pyzhev (107), in 1940. The use of programmed control to increase the production rate per unit reactor volume is considered in some detail by Denbigh (4) in an article published in 1944. In a 1957 paper, Denbigh (108) considers the problem of competing reactions in a series of stirred autoclaves. He showed that, under some circumstances, optimal temperature sequences may be found which maximize the chemical efficiency or yield of the main reaction.

Bilous and Amundson (109) used a piston-flow model for predicting optimal temperature profiles for competing reactions in tubular reactors. Two elegant methods based on functional analysis were presented, and the differential equations that describe the optimum profile were obtained for several specific reaction complexes. One example of their results will be given.

They considered the system of consecutive reactions,

$$A \rightarrow B \rightarrow C \tag{50}$$

where B is the desired product. The kinetics of these two reactions were represented by the equations

$$\frac{dC_a}{dt} = -f(T)\, C_a, \qquad \frac{dC_b}{dt} = f(T)\, C_a - g(T)\, C_b \tag{51}$$

where C_a and C_b are the concentrations of A and B, respectively, $t = x/\bar{u}$, and f and g are the temperature-dependent parts of the rate coefficients. The functional, $H(T)$, was defined by

$$H(T) = \frac{g'_T(T)}{f'_T(T)} \tag{52}$$

where the combination of a prime and a subscript T indicated a functional derivative with respect to the function, $T(t)$. Then the equation for the optimal temperature profile was found to be

$$\frac{d^2T}{dt^2} - \frac{f(T) - J'_T(T)}{J(T)} \left(\frac{dT}{dt}\right)^2 + [f(T) - g(T)] \frac{dT}{dt} = 0 \tag{53}$$

where

$$J(T) = \frac{g(T) - f(T)\, H(T)}{H'_T(T)}$$

In a companion paper, Bilous and Amundson (110) apply the general results of their analysis to the four cases of equation 50 where the reactions are either first or second order. The differential equations

were solved for a wide range of initial conditions by means of an electronic analog computer. The general results were presented graphically in 18 figures. In addition, optimum temperature and concentration profiles were discussed in two specific examples.

Aris (111) attacks the problem of Bilous and Amundson using dynamic programming instead of variational methods. He points out that dynamic programming has a distinct advantage for engineering problems because arbitrary constraints for dependent variables may be introduced into the problem in a very natural way. For examples of such constraints, definite limits to temperatures, pressures, and heat transfer rates may be imposed for reasons of safety and economics. In a subsequent paper, Aris (112) made a complete study of this problem for a single, reversible, first-order reaction.

In recent years, Horn and co-workers have been actively working on optimization problems. In 1959, Horn and Kuechler (80) described methods for determining the optimum temperature profiles in tubular reactors for reactions having the stoichiometric schemes:

$$A \underset{\leftarrow}{\overset{\rightarrow}{}} B$$

$$A + B \rightarrow C + D$$

$$A \rightarrow \begin{matrix} B \\ \searrow\ C \end{matrix}$$

$$A \rightarrow B \rightarrow C$$

In 1960, Horn and Troltenier (113) reported an investigation of a reaction complex having the stoichiometric scheme,

$$\begin{array}{ccccc} A_1 & \rightarrow & A_2 & \rightarrow & A_3 \\ \downarrow & & \downarrow & & \\ A_4 & & A_5 & & \end{array}$$

in which A_3 is the desired product. Optimal temperature profiles were obtained for a piston-flow model of a tubular reactor. These optimum profiles were described by a system of differential equations, and solutions were obtained by numerical methods. Optimization by the method of steepest ascent was also discussed. Two other recent contributions by Horn (114, 115) deal with same subject.

Van de Vusse and Voetter (116) considered optimum pressure and concentration gradients in piston-flow models of tubular and "cross-stream" reactors for the stoichiometric equations,

$$A \rightleftarrows B$$

and

$$A + B \rightarrow C$$

$$A + A \rightarrow D .$$

An approximation was made to reduce the variational problem to an ordinary extreme value problem. This was solved for several important cases by means of an electronic analog computer.

Mathematics

The mathematical contributions on which the theoretical part of this investigation is based deserve some consideration. These contributions fall in three categories: mathematical descriptions of chemically reacting fluids, techniques of numerical analysis, and mathematical questions connected with numerical solutions.

Descriptions of Chemically Reacting Fluids.--Mathematical descriptions for a fluid in which a chemical reaction occurs have been provided by several authors.

Bosworth (117) presented the three equations for conservation of mass, momentum, and energy in a discussion of chemical similarity.

Chambré (100) gave a description of a reacting gas in a tubular reactor. In this formulation it was assumed that the exterior forces acting on the components are equal, pressure and thermal diffusion effects are negligible, the components have identical "Maxwell diffusion coefficients," the gas mixture is ideal, the pressure and dissipation effects are negligible, the Lewis number of the gas equals unity, the properties in the transport equations are constant, and the specific heats of all components are equal. The differential equations of this description were

$$L(\epsilon_j) = \beta \nu_j M_j J(\epsilon_j, T), \qquad j = 1, \ldots, N$$
$$L(h) = 0 \tag{54}$$

where the operator $L(\ )$ is defined as

$$L(\ ) = f_c(s) \frac{\partial(\ )}{\partial \zeta} - \frac{1}{s} \frac{\partial}{\partial s} \left(s \frac{\partial(\ )}{\partial s} \right) \tag{55}$$

and where $\beta = r_w^2 / D\rho$, $\zeta = x / 2D\bar{u}r_w^2$, and $f_c(s) = u(s) / 2\bar{u}$. The $\epsilon_j(s, \zeta)$, ν_j, and M_j are the mass fraction, stoichiometric coefficient, and molecular mass, respectively, of the j^{th} component. The quantity, $J(\epsilon_i, T)$, is the rate of chemical reaction and $h(s, \xi)$ is the specific enthalpy of the system. The boundary conditions were as follows:

1. Prior to initial boundary, $\zeta < 0$

$$\epsilon_j(s, \zeta) = \epsilon_{oj}, \quad \text{constants for } j = 1, \ldots, N$$
$$h(s, \zeta) = h_o, \quad \text{a constant} \tag{56}$$

2. at the tube wall, $s = 1$, $\zeta > 0$

$$\frac{\partial \zeta_j}{\partial s}(1, \zeta) = 0, \quad j = 1, \ldots, N$$
$$h(1, \zeta) = h_w(\zeta) \tag{57}$$

or $$\frac{\partial h}{\partial s}(1, \zeta) = -\frac{Z\, r_w q_w(\zeta)}{k_R}$$

where q_w is a heat flux.

3. at the center line of the tube, $s = 0$, $z > 0$

$$\frac{\partial \zeta_j}{\partial s}(0, \zeta) = 0, \quad j = 1, \ldots, N$$
$$\frac{\partial h}{\partial s}(0, \zeta) = 0 \tag{58}$$

Bird, Stewart and Lightfoot (118) gave a general description of a fluid in which a chemical reaction occurs. Their development permits the equations of change to be written in a variety of equivalent ways, depending on the choices of units and coordinate systems.

Prager (119) presented a general description of a chemically reacting fluid and a number of simplified descriptions applying to special cases.

None of the authors mentioned in this subsection specified the form of the rate functions to be used in their descriptions. According to Benson (120) the accuracy of the usual Arrhenius form of the temperature dependent part of the rate coefficient, e^{-E/R_gT}, is adequate for the accuracy usually attained in kinetic measurements. However, he points out that the form $T^{A_R/R_g}\ e^{-E/R_gT}$ gives better results for some reactions. Murdoch and Holland (85) find the form, e^{aT}, to be a useful simplifying approximation. The latter form also was used by Barkelew (121) with good results.

Methods of Numerical Analysis.--There are ordinarily two steps in the solution of boundary value problems by numerical analysis. The first step is the discretization of the independent variables to obtain an approximate boundary value problem where all derivatives have been replaced by finite-difference quotients. This approximate problem is expressed by algebraic equations that permit the calculation of discrete values of the dependent variables from the given boundary data. The second step is the stepwise computation that generates a set of values of the dependent variables at discrete points throughout the region in which the solution is defined.

A radial-diffusion model of a tubular reactor gives a boundary value problem that involves a system of non-linear partial differential equations of the parabolic type. A listing of the various numerical approximations that have been used for this type of problem and a discussion of their advantages and disadvantages is beyond the scope of this thesis. The reader is referred to the recent books of Richtmeyer (122), Collatz (123) and Forsythe and Wasow (124) for such lists and discussions. An interesting innovation for parabolic partial differential equations that will not be found in these books was recently developed by Varga (125).

Problems of Numerical Solutions.--In all but the simplest cases, the solution of a boundary value problem by numerical analysis raises some vexing questions. If it is assumed that a solution to the original boundary value problem exists, there still remain three questions:

1. How may the solution to the approximate problem be obtained? Even though the equations are algebraic, this may cause some difficulty. For example, in some iterative methods for solving non-linear algebraic equations, the sequence of computed values does not always converge to the solution.

2. Can an approximate solution to the approximate boundary value problem be computed using a finite number of digits in the arithmetic operations? This question is concerned with the stability of the solution to the introduction of small errors and with the accumulation of round-off errors.

3. Can the difference between the solution to the original boundary value problem and the approximate boundary value problem be made small in some sense? This question concerns the convergence of the solution of the latter problem to the solution of the former as the mesh lengths of the finite-difference grid lines approach zero and the difference quotients approach their corresponding derivatives.

These questions are discussed in detail for linear problems by Richtmeyer (122), Forsythe and Wasow (124) and Douglas (126). Several authors also attack these questions for non-linear equations. Three of these investigations are mentioned below.

Douglas (127) considers the quasilinear problem:

$$\frac{\partial^2 v}{\partial s^2} = F(s, z, v)\frac{\partial v}{\partial z} + G(s, z, v) \tag{59}$$

$$F \geq m > 0$$

$$v(s, 0) = f(s), \quad 0 \leq s \leq 1$$

$$v(0, z) = g_1(z), \quad 0 < z \tag{60}$$

$$v(1, z) = g_2(z), \quad 0 < z$$

He approximates 59 and 60 by

$$\Delta^2_{w_{i,n+1}} = F(s_i, z_{n+1}, w_{i,n})\frac{w_{i,n+1} - w_{i,n}}{\Delta z} + G(s_i, z_{n+1}, w_{i,n}), \quad n \geq 0 \tag{61}$$

and

$$w_{i,o} = v(s_i, 0) = f(s_i)$$

$$w_{o,n} = v(0, z_n) = g_1(z_n), \quad w_{I,n} = v(1, z_n) = g_2(z_n) \tag{62}$$

where $I\Delta s = 1$, $w_{i,n}$ indicates the value of w at $s = s_i$ and $z = z_n$, and $\delta^2 w_{i,n} = (w_{i+1,n} - 2w_{i,n} + w_{i,n-1}) / (\Delta s)^2$

Douglas assumes that a solution, $v(s, z)$, to 59 and 60 exists, that d^4v/ds^4 and d^2v/dz^2 exist and are bounded, and that F and G have bounded first derivatives with respect to v. He shows that the difference between $w_{i,n}$ and $v(s_i, z_n)$ is less than $C\, z_n e^{Czn} (\Delta z)^{\beta}$ where $\Delta s = A(\Delta z)^{\alpha}$ and $\beta = \min(1, 2\alpha)$ for C and A constant.

Rose (128) considered the more general problem

$$\begin{aligned} \frac{\partial^2 v}{\partial v^2} &= F\left(s, z, v, \frac{\partial v}{\partial s}, \frac{\partial v}{\partial z}\right) \\ -\beta_0(s)\, v(s, 0) &= f_0(s) \\ \alpha_1(z) \frac{\partial v}{\partial s}(0, z) - \beta_1(z)\, v(0, z) &= g_1(z) \\ \alpha_2(z) \frac{\partial v}{\partial s}(1, z) - \beta_2(z)\, v(1, z) &= g_2(z) \end{aligned} \tag{63}$$

He found that the solution to an approximate problem formulated by him converged uniformly to the solution to the above problem provided that

$$\frac{\Delta z}{(\Delta s)^2} \leq \frac{\partial F}{\partial\left(\frac{\partial v}{\partial z}\right)} \cdot \frac{1}{\eta_2} \tag{64}$$

where $\partial^2 w/\partial s^2$ is approximated by

$$\eta_1 \Delta_s^2 w_{i,n+1} + \eta_2 \Delta_s^2 w_{i,n}, \qquad 0 \leq \eta_2 \leq 1,$$

and

$$\eta_1 + \eta_2 = 1$$

Lees (129) considered a boundary value problem that was similar in some respects to that of Rose:

$$\frac{\partial}{\partial s}\left[p(s,\ z)\ \frac{\partial v}{\partial s}\right] = F\left(s,\ z,\ v,\ \frac{\partial v}{\partial s},\ \frac{\partial v}{\partial z}\right)$$

$$\begin{aligned} v(s,\ 0) &= f_o(s) \\ v(0,\ z) &= g_1(z) \\ v(1,\ z) &= g_2(z) \end{aligned} \tag{65}$$

Three approximate boundary value problems are considered by Lees. These are based on a modified backward difference equation, a difference equation due to Rose, and a Crank-Nicolson type of difference equation. The first of these was written as

$$\nabla_s\left[p\left(s+\frac{\Delta s}{2},z\right)\ \Delta_s w_{i,n+1}\right] = F\left[s_i, z_n, w_{i,n}, \tfrac{1}{2}\left(\Delta_s w_{i,n} + \nabla_s w_{i,n}\right),\ \nabla_z w_{i,n+1}\right]$$

$$\begin{aligned} w_{i,o} &= v(s_i,\ 0) = f_o(s_i) \\ w_{o,n} &= v(0,\ z_n) = g_1(z_n) \\ w_{I,n} &= v(1,\ z_n) = g_2(z_n) \end{aligned} \tag{64}$$

where $\nabla_s w_{in} = (w_{i,n} - w_{i-1,n})/\Delta s$

and $\Delta_s w_{in} = (w_{i,n+1} - w_{i,n})/\Delta s$

Lees shows that the largest value of $|v - w|$ converges to zero in the region of definition of v. No restriction was placed on the ratio, $\Delta z/(\Delta s)^2$. The assumptions were as follows:

1. The solution, $v(s, z)$, exists and has derivatives in its region of definition.

2. The function, $p(s, z)$ has bounded third derivatives in its region of definition and satisfies $0 < p_1 < p(s, z) < p_2$ for some constants, p_1 and p_2.

3. The function $F(s, z, x_1, x_2, x_3)$ has at least one bounded derivative with respect to x_1, x_2, and x_3 and there are constants, a_1 and a_2, such that

$$0 < a_1 \leq \frac{\partial F}{\partial x_3} \leq a_2$$

for all values of x_1, x_2, and x_3.

For non-linear equations, Lees developed an iterative method of solution of the approximate boundary value problem and thereby showed the existance and uniqueness of the solution to this problem.

CHAPTER III

THEORETICAL INVESTIGATION

This chapter deals with the formulation of a general boundary value problem as a mathematical model of a tubular reactor and with calculations based on a particular boundary value problem. This particular problem is obtained by specifying boundary conditions and an expression for the reaction rate. Finally, a numerical method for the solution of the particular boundary-value problem is presented.

A Mathematical Model

In Chapter II several mathematical models for tubular reactors were discussed and compared. A radial-diffusion model will be used here. The assumptions of this model have been presented toward the beginning of this section, but the discussion of these assumptions is deferred until all the equations of the model have been presented.

Differential Equations.--Bird, Stewart, and Lightfoot (130) have written the basic differential equations describing a chemically reacting fluid. These have been simplified by the following assumptions:

1. Variations in the fluid properties ρ, ν, K_m and Z are negligible,

2. a steady state exists,

3. the velocity and diffusivity distributions do not change with respect to displacement in the direction of the axis of the tube,

4. the radial and tangential components of the temporal-mean velocity are negligible,

5. diffusion in the axial and tangential directions is negligible,

6. heat generated by viscous dissipation is negligible,

7. thermal and pressure diffusion are negligible,

8. external forces (gravitational, electrical, magnetic, etc.) act equally on all components of the reaction mixture,

9. the effective binary diffusivities of all components are equal, and

10. the transport of energy by diffusion of mass is negligible by comparison with the other terms in the energy equation.

Under these assumptions, the energy equation for a mixture with a single reaction may be written

$$\frac{1}{r}\frac{\partial}{\partial r}\left[rK(r)\frac{\partial T}{\partial r}\right] - u\frac{\partial T}{\partial x} - \frac{H_R U(c,T)}{Z\rho} = 0 \qquad (67)$$

and the equation of continuity for the i^{th} constituent of the reaction mixture may be written

$$\frac{1}{r}\frac{\partial}{\partial r}\left[rD(r)\frac{\partial c_i}{\partial r}\right] - u\frac{\partial c_i}{\partial x} + \frac{\nu_i U(c,T)}{\rho} = 0 \qquad (68)$$

where D is an effective binary diffusivity and the dimension of c is moles per unit mass. The reaction rate expression, U, is shown only in symbolic form here for generality.

Equation 1, the stoichiometric equation for a single reaction,

may be written

$$\sum_{i}^{I} \nu_i M_i = 0, \qquad i = 1,2, \ldots, I \tag{69}$$

where M_i and ν_i are the molecular weight and stoichiometric coefficient of the i^{th} component. The coefficient ν_i is negative, positive, or zero if the i^{th} component is a reactant, a product or an inert, respectively, Prigogine and Defay (131) define the "extent of reaction," ξ, for a closed system by

$$c_i - c_i^o = \nu_i \xi. \qquad i = 1, \ldots, I \tag{70}$$

where c_i^o and c_i are the number of moles of the i^{th} component corresponding to the initial composition of some mixture and to the composition of the same mixture after an extent of reaction, ξ. For an open system the dimension of equation 70 is interpreted as moles per unit mass. Then, equation 68 can be written for the j^{th} reaction as

$$\frac{1}{r} \frac{\partial}{\partial r} \left[rD(r) \frac{\partial \xi_j}{\partial r} \right] - u \frac{\partial \xi_j}{\partial x} + \frac{U_j(\xi,T)}{\rho} = 0 \tag{71}$$

where $U_j = \rho \, d\xi_j/dt$ in a closed, perfectly-mixed system. Note that equation 71 is independent of the component and that it has been written for components that take part in no more than one reaction. Thus, only one equation of the form of 71 and one reference composition are needed to describe the composition of a reacting fluid in which a single reaction occurs.

If more than one reaction occurs in the fluid, equation 69 becomes

$$\sum_{i}^{I} \nu_{ij} M_i = 0, \qquad j = 1, \ldots, J \tag{72a}$$

for J reactions. This may be written in matrix notation as

$$[\nu] \vec{M} = 0 \tag{72b}$$

where $[\nu]$ is a J by I matrix and $\vec{M}$ is a column vector of I elements. According to Prigogine and Defay (132), Jouguet's criterion states that the number of independent reactions is equal to the rank of the matrix $[\nu]$. For each independent reaction, an extent of reaction may be defined and an equation analogous to 71 may be written. In case a component of the reaction mixture takes part in more than one independent reaction, at least one of the equations analogous to 71 will contain more than one U.

Equations 67 and 68 can be written in another convenient form by defining the variable Υ,

$$\Upsilon = \frac{c_1}{c_1^o}$$

where c_1 is the concentration of the stoichiometrically limiting reactant. Then for the n^{th} reactant

$$\frac{c_n}{c_1^o} = \frac{\nu_n}{\nu_1} [\Upsilon + \Delta_{sn}] \tag{73}$$

where $$\Delta_{sn} = \frac{\nu_1 c_n^o - \nu_n c_1^o}{\nu_n c_1^o} \quad .$$

The equations may also be made dimensionless by the procedure of inspectional analysis described by Birkhoff (133). This consists in a change of variable:

$$\theta = TR_g / E, \quad s = r / r_w, \quad z = x / L, \quad \hat{u}(s) = U(s) / \bar{u} ,$$

$$\hat{K}(s) = K(s) / K^*, \quad \hat{D}(s) = D(s) / D^*, \quad R(\gamma,\theta) = U(\gamma,\theta) / U^*,$$

where U^*, K^*, and D^* are characteristic values of these variables. For example, K^* might be chosen as K_m or the least upper bound of $K(s)$ for constant Reynolds number. When these new variables are substituted into equations 67 and 68, they become

$$\left(\frac{LK^*}{\bar{u}r_w^2}\right) \frac{1}{s} \frac{\partial}{\partial s} \left[s\hat{K}(s) \frac{\partial\theta}{\partial s}\right] - \hat{u} \frac{\partial\theta}{\partial s} - \left(\frac{R_g L H_R U^*}{E\bar{u}Z\rho}\right) R(\gamma,\theta) = 0 \qquad (75)$$

$$\left(\frac{LD^*}{\bar{u}r_w^2}\right) \frac{1}{s} \frac{\partial}{\partial s} \left[s\hat{D}(s) \frac{\partial\gamma}{\partial s}\right] - \hat{u} \frac{\partial\gamma}{\partial s} + \left(\frac{LU^*}{\rho\bar{u}}\right) R(\gamma, \theta) = 0 \qquad (76)$$

Boundary Conditions.--One of the difficulties in the theory of industrial reactions, as described in Chapter II, is the mathematical formulation of realistic boundary conditions for reactors. The corresponding experimental problem is to choose boundary conditions that are as close as possible to practical industrial conditions and that, at the same time, allow accurate mathematical representation.

In the case of homogeneous reactions in tubular reactors, the reaction may be initiated by mixing the reactants together at the reaction

temperature, by adding a homogeneous catalyst or free-radical initiator to the reaction mixture, by increasing the temperature of the mixture, or by subjecting the mixture to photolysis. The radial-diffusion model used here is unsatisfactory for the entrance section of the reactor in the first two of these cases. This is so, because the presence of radial and tangential components of velocity and the variation of $u(s)$ as a function of z are contrary to the assumptions of the model. However, even in these two cases, if the concentration and temperature distributions are known at some point, z_o, where the assumptions concerning velocity are legitimate, then the model can be used to describe the reaction mixture downstream from z_o. Throughout this investigation, whenever a reaction is initiated by the admixture of a reactant or catalyst, it is assumed that the concentration or temperature profiles at z_o are known from experimental measurements or have been estimated using another model for the initial section of the reactor. Thus, two of the boundary conditions for the theoretical part of this work are

$$\theta(s,0) = f_1(s) \quad \text{and} \quad \gamma(s,0) = f_2(s) \tag{77}$$

where $\theta(s,z)$ and $\gamma(s,z)$ are the functions satisfying equations 75 and 76 and z_o has been taken as the origin of the z coordinate.

The conditions at the axis of the reactor tube are

$$\frac{\partial\theta}{\partial s}(0,z) = 0 \quad \text{and} \quad \frac{\partial\gamma}{\partial s}(0,z) = 0 \tag{78}$$

because of the vanishing of radially directed fluxes at $s = 0$. The vanishing of the radially-directed mass flux at the tube wall for all

constituents of the reaction mixture gives

$$\frac{\partial \gamma}{\partial s}(1,z) = 0 \tag{79}$$

The conditions for θ at the tube wall require the consideration of four possibilities:

$$\theta(1,z) = g_1(z) \tag{80a}$$

$$\frac{\partial \theta}{\partial s}(1,z) = g_2(z) \tag{80b}$$

$$\frac{\partial \theta}{\partial s}(1,z) + A_1(z)\,\theta(1,z) = A_2(z)\,g_3(z) \tag{80c}$$

$$\frac{\partial \theta}{\partial s}(1,z) + B(z)\,\theta^4(1,z) = B(z)\,g_4(z) \tag{80d}$$

The conditions of uniform wall temperature and uniform wall heat flux are special cases of equations 80a and 80b. Equation 80d describes the heating of the reactor tube by radiant energy. Equation 80c is a generalization that gives 80b if $A_1 = 0$ and approximates 80a if $A_1 = A_2 \gg 1$. If $A_1 = A_2 = A_x(z)$, equation 80c describes the exchange of heat through the reactor wall between an external fluid and the reaction mixture. In this case, A_x is an "external Nusselt number," $(h_{Tx} r_w)/ k_{Tw}$ and $\theta_J(z) = g_3(z)$ is the mean value of the dimensionless temperature of the external fluid. The heat transfer coefficient h_{Tx} is defined by equation 80c and k_{Tw} is the thermal conductivity at the tube wall, that is, the molecular thermal conductivity of the fluid.

Velocity and Eddy Diffusivity Distributions.--An essential part of this model of tubular reactor is the specification of velocity and diffusivity

distributions. In view of the quantity of work and number of publications on these subjects, the specification of these distributions was not expected to be a problem. However, a number of published velocity correlations were judged by the seven criteria listed in Chapter II and were found to be unsatisfactory for Reynolds numbers between 3,000 and 50,000. Since the theoretical calculations were to be compared with experimental results, it was necessary to find or develop a velocity correlation that would be satisfactory for the values of Reynolds number used in the experimental part of this study. For the sake of consistency, it was decided to obtain the eddy diffusivity distribution from the velocity distribution or vice versa so that these were not considered separately. Thus, the search for a satisfactory velocity distribution became a necessary adjunct to the original problem of this investigation. The approach to this subsidiary problem was strictly empirical: any velocity correlation, regardless of origin, that satisfied the seven criteria listed in Chapter II would be considered satisfactory.

Before considering two proposed velocity distributions, the derivation of some useful equations will be outlined below.

Under the assumptions of this chapter, the time-averaged equation of motion reduces to

$$\frac{\tau g_c}{\rho} = \frac{r}{2} \frac{g_c}{\rho} \left(- \frac{dP}{dx} \right) \tag{81}$$

where τ is the shear stress in the fluid and $-dP/dx$ is the pressure gradient. The eddy diffusivity of momentum, ε_v, is defined by

$$\frac{\tau g_c}{\rho} = - (\nu + \varepsilon_v) \frac{du}{dr} = (\nu + \varepsilon_v) \frac{du}{dy} \tag{82}$$

where u is the temporal-mean velocity in the axial direction and $y = r_w - r$. Prandtl's mixing length, ℓ_p, is defined by

$$\varepsilon_v \frac{du}{dy} = \ell_p^2 \left|\frac{du}{dy}\right| \frac{du}{dy}$$

or, since du/dy is non-negative throughout the range of y considered,

$$\varepsilon_v \frac{du}{dy} = \ell_p^2 \left(\frac{du}{dy}\right)^2 \tag{83}$$

The pressure is assumed constant throughout a tube cross section, so from a force balance

$$\frac{\tau}{\tau_w} = \frac{r}{r_w} \tag{84}$$

The friction factor, f_F, is defined by

$$f_F = \frac{r_w g_c}{\bar{u}^2 \rho} \left(-\frac{dP}{dx}\right) = \frac{2\tau_w g_c}{\bar{u}^2 \rho} \tag{85}$$

Also, as a matter of notation, other variables are introduced by the following definitions:

$$\hat{u} = \frac{u}{\bar{u}}, \quad u^* = \sqrt{\frac{\tau_w g_c}{\rho}} = u\sqrt{\frac{f_F}{2}}, \quad u^+ = \frac{u}{u^*},$$

$$y' = \frac{Y}{r_w} = \frac{r - r_w}{r_w}, \quad y^+ = \frac{yu^*}{\nu} = y' \frac{N_{Re}}{2} \sqrt{\frac{f_F}{2}},$$

$$Y^+ = \frac{r_w u^*}{\nu}, \quad s = \frac{r}{r_w} = 1 - \frac{y^+}{Y^+} = 1 - y'. \tag{86}$$

From 82 and 83

$$\ell^2 \left(\frac{du}{dy}\right)^2 + \frac{du}{dy} = \frac{\tau g_c}{\rho} = \frac{\tau_w g_c s}{\rho} \tag{87}$$

or

$$\frac{N_{Re}}{2}\left(\frac{\ell_P}{r_w}\right)^2 \left(\frac{d\hat{u}}{dy'}\right)^2 + \frac{d\hat{u}}{dy'} - \frac{N_{Re} f_F s}{4} = 0$$

Then, since $w = \dfrac{-2c}{b + \sqrt{b^2 - 4ac}}$ is a solution of $aw^2 + bw + c = 0$,

$$\frac{d\hat{u}}{dy'} = \frac{\frac{1}{2} N_{Re} f_F s}{1 + \left[1 + \frac{1}{2} N_{Re}^2 f_F s \left(\frac{\ell_P}{r_w}\right)^2\right]^{\frac{1}{2}}} \tag{88a}$$

or

$$\frac{du^+}{dy^+} = \frac{2s}{1 + \left[1 + r\left(\frac{y^+ \ell_P}{r_w}\right)^2\right]^{\frac{1}{2}}} \tag{88b}$$

The integral form of 88b is

$$u^+ = \int_0^{y^+} \frac{2\left(1 - \frac{y^+}{Y^+}\right)}{1 + \left[1 + r\left(\frac{y^+ \ell_P}{r_w}\right)^2 \left(1 - \frac{y^+}{Y^+}\right)\right]^{\frac{1}{2}}} \tag{89}$$

From 82, 84, 86, and 88b,

$$\frac{\varepsilon_v}{\nu} = \frac{2\left(\frac{y^+ \ell_P}{r_w}\right)^2 s}{1 + \left[1 + 4\left(\frac{y^+ \ell_P}{r_w}\right)^2 s\right]^{\frac{1}{2}}} \tag{90a}$$

or

$$\frac{\varepsilon_v}{\nu} = \frac{1}{2}\left\{-1 + \left[1 + 4\left(\frac{Y^+ \ell_p}{r_w}\right)^2 s\right]^{\frac{1}{2}}\right\} \qquad (90b)$$

The satisfaction of several of the seven criteria by the Gill and Scher (49) modification of Van Driest's (47) correlation suggested that further modification might give a very satisfactory velocity distribution. The Gill and Scher expression for ℓ_p / r_w, equation 14, was modified to read

$$\frac{\ell_p}{r_w} = K_v \frac{y^+}{Y^+}\left[\exp\left(\frac{p_1 y^+}{Y^+}\right) - \exp\left(\frac{p_2 y^+}{Y^+}\right)\right] \qquad (91)$$

where the parameters p_1 and p_2 are empirical functions of Reynolds number. The insertion of this expression in equations 89 and 90 allows the computation of velocity and diffusivity distributions. Two sets of parameters were found for these equations, namely

$$K_v = 0.4, \quad p_1 = -0.3 - 0.0695 \ln N_{Re} \qquad (92a)$$

$$p_2 = 1.0 - 0.006355\, N_{Re}^{0.8308}$$

and

$$K_v = 0.36, \quad p_1 = -0.75 + \frac{71}{N_{Re} - 3580} \qquad (92b)$$

$$p_2 = 2.0 - 0.0082296\, N_{Re}^{0.82242}$$

The velocity profiles for Reynolds numbers from 5,000 to 100,000 were very nearly the same for the two sets of parameters shown above.

The reader will recall from Chapter II that one of the objectives to the correlation of Gill and Scher is the fact that a graph of u^+

versus $\log y^+$ is concave downwards throughout the interval $\log 30 \leq \log y^+ \leq \log Y^+$. In contrast, most experimental profiles for Reynolds numbers greater than about 8,000 appear to be concave upwards over a large part of this interval. In brief, this correlation does not have the proper shape to agree with experimental data over the entire interval $0 \leq \log y^+ \leq \log Y^+$ and must fail to satisfy either criterion (2) or (4). This defect is less pronounced in the profiles given by equations 91, 92a, and 92b, that is, the curves are less concave downwards. However, the shape defect is still present to an undesirable degree. The reader should note that the unusual advantage, present in Gill and Scher's work, of agreement with the Hagen-Poiseuille equation at low Reynolds numbers has been lost. Also, the eddy diffusivity given by a combination of 91 and 90 gives $\varepsilon_v = 0$ at $s = 0$, that is, criterion (7) is not satisfied. In view of these and other deficiencies, the correlation given by equations 89 and 91 was judged unsatisfactory for use in this thesis.

Another improved velocity correlation was suggested by the following equation of Ruth and Yang (45),

$$\sqrt{\frac{\tau g_c}{\rho}} \doteq \ell_p \frac{du}{dy}, \qquad \nu \ll \varepsilon_v \tag{93}$$

which may be obtained from 82 and 83. Starting from this, 83, 84, and 85 give

$$\frac{\varepsilon_v}{\nu} \doteq \frac{\ell_p}{r_w} Y^+ \frac{r}{s^2} \tag{94}$$

The substitution of 94 into 88b gives

$$\frac{du^+}{dy^+} \doteq \frac{2s}{1 + \left[1 + 4\left(\frac{\varepsilon_v}{\nu}\right)^2\right]^{\frac{1}{2}}}, \qquad \nu \ll \varepsilon \tag{95}$$

This suggests the possibility of finding some function, $\varphi(y^+)$, such that

$$\frac{du^+}{dy^+} = \frac{2s}{1 + \left[1 + 4\varphi^2\right]^{\frac{1}{2}}} \tag{96}$$

regardless of the relative size of ε_v and ν. If one assumes that such a function can be found, a comparison of equations 96 and 88b yields

$$\varphi^2 = \left(\frac{Y^+ \ell_p}{r_w}\right)^2 s \tag{97}$$

and equation 90a becomes

$$\frac{\varepsilon_v}{\nu} = \frac{2\varphi^2}{1 + \left[1 + 4\varphi^2\right]^{\frac{1}{2}}} \tag{98}$$

For $\varepsilon_v \gg \nu$, 94 and 95 give

$$\frac{\varepsilon_v}{\nu} \doteq \varphi, \qquad \varepsilon_v \gg \nu \tag{99a}$$

or

$$\frac{\varepsilon_v}{r_w u^*} = \frac{\varphi}{Y^+}, \qquad \varepsilon_v \gg \nu \tag{99b}$$

and, since for $\varepsilon_v \ll \nu$, 82, 83, 84, and 85 yield

$$\frac{\varepsilon_v}{\nu} \doteq \frac{N_{Re}^2}{8} f_F \left(\frac{\ell_p}{r_w}\right)^2$$

one sees that

$$\frac{\varepsilon_v}{\nu} \doteq \frac{\varphi^2}{s}, \quad \varepsilon_v << \nu \tag{100a}$$

For all except very low Reynolds numbers it is known that $\varepsilon_v << \nu$ holds only for $s \doteq 1$, so under these conditions

$$\frac{\varepsilon_v}{\nu} \doteq \varphi^2, \quad \varepsilon_v << \nu \tag{100b}$$

One possible function that may be used in equation 96 is

$$\varphi = Y^+ \omega_a (y')^{\omega_b} \exp(-\omega_c y') \tag{101}$$

for suitable values of the parameters ω_a, ω_b, and ω_c. The reader should note that Y^+, ω_a, ω_b, and ω_c are all functions of Reynolds number. Incidentally, as $\varepsilon_v \to 0$ for $s \to 1$, 100b and 101 show that

$$\varepsilon_v \sim (y')^{2\omega_b} \tag{102}$$

Equation 98 shows that criterion (7) is satisfied and for the choice of φ given by 101, equation 96 shows that criteria (5) and (6) are satisfied. Inspection of 101 shows that criterion (3) can be satisfied qualitatively, at least. The judgement of this correlation according to criteria (1), (2), (3), and (4) requires the specification of the parameters ω_a, ω_b, and ω_c. For the purposes of this investigation,

these were related to Reynolds number by

$$\left.\begin{aligned} \omega_a &= 12.82 - 0.91 \log N_{Re} - 3.8 \times 10^7 N_{Re}^{-2.097} \\ \omega_b &= 1.45 + 59.305 N_{Re}^{-0.5163} \\ \omega_c &= \frac{1}{0.175 + 9.508 N_{Re}^{-0.6266}} \end{aligned}\right\} \qquad (103)$$

These expressions are not claimed to be the best or the simplest of possible relations. They represent a compromise for a range of Reynolds numbers from 3,000 to 50,000. Better values of the parameters can be found for narrower ranges of the Reynolds number.

Comparisons of the proposed correlation with experimental velocity data for Reynolds numbers of 5,000, 10,000, 19,000, and 39,500 are presented in Figures 5, 6, 7, and 8, respectively. The first three figures show that a velocity distribution computed from equations 96 and 101 is capable of reproducing the shape of experimental velocity profiles. The computed distributions do not agree with all sets of data, but by adjusting the values of the parameters ω_a, ω_b, and ω_c in equation 101, good agreement can be obtained for any particular set of data within a wide range. If this is done, the satisfaction of criteria (2) and (4) by the resulting velocity distribution depends on the accuracy and consistency of the experimental data.

At larger values of Reynolds number it becomes increasingly difficult to obtain the correct derivative, $\frac{du^+}{d(\log y^+)}$, in the interval $\log 30 \leq \log y^+ \leq \log Y^+/2$ and simultaneously satisfy criterion (4). This is shown by Figure 8. The computed distribution can be improved

by other choices of the values of ω_a, ω_b, and ω_c for higher Reynolds numbers, but in general the correlation is unsatisfactory for use above a Reynolds number of 50,000.

An examination of Table 2 shows that the proposed velocity distribution is reasonably consistent with respect to the mean velocity $\bar{u}$. In particular, this velocity distribution is much better than the other two distributions for Reynolds numbers less than 10,000.

Table 3 gives a comparison between values of $\bar{u}/u_{max}$ from the proposed distribution, three other velocity distributions, and two correlations of a large number of experimental $\bar{u}/u_{max}$ data. The agreement of the proposed distribution with the two correlations of experimental data is very good for all values of Reynolds number from 3,000 to 50,000. The relations between ε_v/ν and s and between ℓ_p/r_w and s are shown in Figures 9 and 10 for typical values of Reynolds number.

In summary, the proposed velocity distribution satisfies all seven of the criteria of Chapter II over a moderate range of Reynolds number. Although the distribution is not satisfactory for values of Reynolds number greater than 50,000, it is the best available distribution for the purposes of this investigation.

Eddy Diffusivities of Heat and Mass.--Eddy diffusivities of heat and mass, ε_H and ε_M, have been defined by equations analogous to 82. As an example, Sherwood (10) may be cited. The diffusivities in these defining equations can be evaluated from experimental measurements or from relations connecting the diffusivities to other quantities such as the eddy diffusivity of momentum. As mentioned in Chapter II, various authors have proposed to relate the ratios $\varepsilon_H/\varepsilon_v$ and $\varepsilon_M/\varepsilon_v$ to

Table 2. Consistency of Velocity Correlations

$N_{Re} \times 10^{-3}$	Ratio of the Value of $\bar{u}$ Obtained by Integrating to the Original Value of $\bar{u}$		
	Proposed Correlation, Equations 96, 101, 103	Universal Velocity Profile, Eq. 7	Deissler Equations 11
3	0.976		
4	0.990		
5	0.994	0.952	
6	0.996		
8	0.996		
10	0.994	0.988	0.962
15	0.979		
20	0.989		
25	0.990	1.005	
30	0.988		
40	0.986	1.006	0.999
50	0.985	1.010	
75	0.997		
100	1.001		

Table 3. Comparison of $\bar{u}/u_{max}$ Values

$N_{Re} \times 10^{-3}$	Ratio of $\bar{u}/u_{max}$					
	Velocity		Correlations		Correlations of Experimental $\bar{u}/u_{max}$ Data	
	Proposed Correlation, Eq. 96, 101, 103	Gill and Scher Eq. 14	Un. V. Pr., Eq. 7	Deissler, Eq. 11	Robertson (32)	Rothfus et al. (16)
3	0.728		0.795	0.814	0.725	0.717
4	0.747					0.744
5	0.758	0.790	0.797	0.807	0.759	0.758
6	0.764					0.765
8	0.772		0.800	0.805		0.774
10	0.779	0.825	0.802	0.806	0.779	0.780
15	0.791		0.808	0.808		0.792
20	0.796				0.794	0.798
25	0.800	0.850				0.803
30	0.804		0.821	0.814		0.808
40	0.807				0.808	0.812
50	0.810		0.833	0.823		0.818
75	0.810		0.843	0.832	0.820	
100	0.808		0.853	0.838		0.830

Reynolds number, relative radius, Prandtl or Schmidt number, and ε_v/ν. There are other possibilities. For example, the direction and magnitude of the heat flux might affect the ratio $\varepsilon_H/\varepsilon_v$.

The writer is convinced that ε_H and ε_M are not necessarily equal to ε_v, notwithstanding the popularity of this assumption. Evidence for the non-equality of these quantities is found in the work of Sherwood and Woertz (33), Towle and Sherwood (134), Dhanak (35), Schwarz and Hoelscher (67), Page and co-workers (34), Isakoff and Drew (30), Brown, Amstead, and Short (135), Sleicher (13), and Abbrecht and Churchill (36), not to mention the work cited by Hinze (136) for flow configurations other than pipe and channel flow.

Evidence for the dependence of $\varepsilon_H/\varepsilon_v$ on Reynolds number has been presented by Page and co-workers (34), Sleicher (13), Abbrecht and Churchill (36). The recent work of Flint, Kada, and Hanratty (38) indicates that $\varepsilon_M/\varepsilon_v$ also may be dependent on Reynolds number. On the other hand, no definite relationship between $\varepsilon_M/\varepsilon_v$ and Reynolds number is evident in the work of Sherwood and Woertz (33) or Dhanak (35).

A comparison of heat transfer studies using air and liquid metals indicates that $\varepsilon_H/\varepsilon_v$ is dependent on Prandtl number. As examples, the work of Rohsenow and Cohen (63) and that of Brown, Amstead, and Short (135) may be mentioned. However, confirming evidence for fluids having Prandtl numbers greater than unity appears to be lacking. On the other hand, in the paper of Flint, Kada, and Hanratty (38), values of ε_M for air and water were correlated successfully as a function of Reynolds number without regard to the difference in values of Schmidt

number. In experiments with jets, Hinze and Van der Hegge Zijnen (137) found no difference in ε_M and ε_H in the absence of density effects. Also, according to Hinze (138), the ratio of eddy diffusivities obtained from Forstall and Gaylord's experiments with a submerged water jet is approximately the same as the values obtained using gas jets.

Except for fluids having very low Prandtl numbers, the variation of $\varepsilon_H/\varepsilon_v$ due to Prandtl number does not appear to be large. Since the true relationships are not accurately known, any choice of a connection between $\varepsilon_H/\varepsilon_v$ and Prandtl number is somewhat arbitrary. For the sake of simplicity, the variation of $\varepsilon_H/\varepsilon_v$ with Prandtl number and the variation of $\varepsilon_M/\varepsilon_v$ with Schmidt number are assumed to be negligible.

Evidence for the dependence of $\varepsilon_H/\varepsilon_v$ on relative radius has been given by Page and co-workers (34), Sleicher (13), and Abbrecht and Churchill (36). While this evidence is impressive, in the opinion of the writer it is not conclusive because of the insufficient precision and quantity of the currently available velocity data. As shown in Chapter II and Appendix I, there is a considerable uncertainty in the evaluation of ε_v from available data. Hence, the effect of relative radius is here assumed to be negligible, again for reasons of simplicity.

For the purposes of this investigation, it is assumed that $\varepsilon_H = \varepsilon_M$, and that the ratios $\varepsilon_H/\varepsilon_v$ and $\varepsilon_M/\varepsilon_v$ are dependent on Reynolds number but not on Prandtl number, Schmidt number or relative radius. The assumed relationship between $\varepsilon_H/\varepsilon_v$ and Reynolds number is

$$\frac{\varepsilon_H}{\varepsilon_v} = \frac{\varepsilon_M}{\varepsilon_v} = 2.52 - 0.3 \log N_{Re}, \qquad N_{Re} < 50{,}000 \qquad (104)$$

This relationship was suggested by the values of $\varepsilon_H/\varepsilon_v$ computed by Sleicher (13) and Page, Schlinger, Breaux, and Sage (34) for the portion of the flow remote from the wall.

Discussion of Assumptions.--The ten assumptions used in the formulation of this model of a tubular reactor require some explanatory comment.

It is well known that the molecular properties of a fluid are affected by changes in temperature and composition. Furthermore, the evaluation of these properties as functions of temperature and concentration would not greatly complicate the model described above. However, the inclusion of concentration and temperature-variable properties in the formulation of the model precludes the simplifications leading to equations 67, 68, and 81.

The assumption of negligible axial diffusion is based on Taylor's (68) estimate of the relative importance of true axial diffusion and virtual axial diffusion caused by a combination of radial diffusion and distributed velocity. He found that the former effect is about 200 times smaller than the latter.

The assumption of equal diffusivities is based on the belief that turbulent diffusivities are relatively independent of the molecular properties of the fluid. The experiments of Sherwood and Woertz (33) indicate that his may not be true in fluids of variable density. Of course, very close to the reactor wall where turbulent diffusivities are small compared to molecular diffusivities, this assumption is in error. However, this error is thought to be tolerable in view of the great simplification permitted in the model by this assumption. For

further discussion of turbulent diffusion in multicomponent mixtures, the reader is referred to a paper by Toor (139).

Calculations

Only particular solutions of equations 75 and 76 with boundary conditions were attempted. Some of the difficulties inherent in a general solution may be seen merely by observing the number of variables and parameters. There are two dependent variables, two independent variables and five dimensionless parameters [N_{Re} is an implicit parameter because it affects $\hat{u}(s)$, $\hat{K}(s)$, and $\hat{D}(s)$] in equations 75 and 76. There is one dimensionless parameter in 80c and three variable functions in boundary conditions 77 and 80c. The calculation of particular solutions to this problem over appreciable ranges of these parameters and functions was not practical due to the excessive computer time required and the difficulty in representing the results accurately and compactly.

Expressions for Reaction Rate.--In order to obtain particular solutions, the expression for the reaction rate must be specified in the model. An expression for the rate of the irreversible reaction in which components 1 and 2 are reactants and the remaining components are products, is given by

$$U = U^* k_R'(T)\, \rho^{n+m} \left(\frac{\nu_2}{\nu_1}\right)^m c_1^n \,(c_1 + \delta_s)^m \qquad (105a)$$

where

$$k_R'(T) = e^{B - E/R_g T} \quad \text{and} \quad \delta_s = \frac{\nu_1 c_1}{\nu_2} - c_1^o \,.$$

Equivalent expressions are

$$U = U^{*}K_R'(\theta)\ \rho^{n+m}\ \nu_1^n \nu_2^m\ (\xi + \frac{c_1^o}{\nu_1})^n\ \ (\xi + \frac{c_2^o}{\nu_2})^m \qquad (105b)$$

and

$$U = U^{*}k_R'(\theta)\ (\rho\ c_1^o)^{n+m}\ (\frac{\nu_2}{\nu_1})^m\ \ \gamma^n(\gamma + \Delta_s)^m \qquad (105c)$$

where $k_R'(\theta) = e^{B-1/\theta}$, $\gamma = \frac{c_1}{c_1^o}$, and $\Delta_s = \frac{\nu_1\ c_2^o - \nu_2\ c_1^o}{\nu_2\ c_1^o}$.

Prigogine and Defay (140) point out that one reason for using the equations 71 and 105b, involving the variable ξ, is that ξ is directly related to the production of entropy in a spontaneous change. On the other hand, the equations involving γ are more suitable for comparing different reaction mixtures because the range of γ, $0 \leq \gamma \leq 1$, is the same for all reactions regardless of the composition of the initial mixture or the order of the reaction.

Description of Calculations.--The equations and boundary conditions used for the calculations described in this thesis are

$$\frac{P_1}{s}\frac{\partial}{\partial s}\left[s\ \hat{K}(s)\ \frac{\partial\theta}{\partial s}\right] - \hat{u}(s)\ \frac{\partial\theta}{\partial z} - Q_1R(\gamma,\theta) = 0 \qquad (106a)$$

$$\frac{P_2}{s}\frac{\partial}{\partial s}\left[s\ \hat{D}(s)\ \frac{\partial\gamma}{\partial s}\right] - \hat{u}(s)\ \frac{\partial\gamma}{\partial s} + Q_2(\gamma,\theta) = 0 \qquad (106b)$$

$$\hat{u}(s) = \int_0^{y'} \frac{\frac{1}{2} f_F N_{Re} (1 - y') \, dy'}{1 + [1 + 4\varphi^2]^{\frac{1}{2}}} \tag{106c}$$

$$\hat{D}(s) = \frac{1}{D^*} \left\{ D_m + \frac{M}{2} [(1 + 4^{\,2}) - 1] \right\} \tag{106d}$$

$$\hat{K}(s) = \frac{1}{K^*} \left\{ K_m + \frac{\alpha_H \nu}{2} [(1 + 4\varphi^2)^{\frac{1}{2}} - 1] \right\} \tag{106e}$$

$$\gamma(s, 0) = f_1(s) \qquad \theta(s, 0) = f_2(s) \tag{107a}$$

$$\frac{\partial \gamma}{\partial s} (0,z) = \frac{\partial \theta}{\partial s} (0,z) = 0 \tag{107b}$$

$$\frac{\partial \gamma}{\partial s} (1,z) = 0 \tag{107c}$$

$$\frac{\partial \tau}{\partial s} (1,z) + A[\theta(1,z) - \theta_J(z)] = 0 \tag{107d}$$

where $$P_1 = \frac{LK^*}{\bar{u} r_w^2} , \qquad Q_1 = \frac{R_q L H_R U^*}{E \bar{u} Z \rho} ,$$

$$P_2 = \frac{LD^*}{\bar{u} r_w^2} , \qquad Q_2 = \frac{L U^* \nu_1}{\rho \bar{u} c_1^o} ,$$

$$\frac{U}{U^*} = R(\gamma, \theta) = (c_1^o \rho)^{m+n} \left(\frac{\nu_2}{\nu_1}\right) k_R'(\theta) \gamma^n (\gamma + \Delta_s)^m ,$$

$$\alpha_M = \frac{\varepsilon_M}{\varepsilon_v} , \text{ and } \alpha_H = \frac{\varepsilon_H}{\varepsilon_v} .$$

In these equations, only a single, irreversible reaction is considered. The symbol U* is numerically unity, but carries the

dimensions required by the equation. The quantities D^* and K^* are chosen as the least upper bounds of $D(s)$ and $K(s)$, respectively. The function φ is defined by equation 101 and the parameters in this equation are related to Reynolds number by equation 103. The quantities α_M and α_H are related to Reynolds number by equation 104. The functions $f_1(s)$ and $f_2(s)$ are always interpreted as the constants 1 and $\theta^o = (T^oR_g)/E$, respectively in these calculations, although provisions were made for more general functions.

Some of the calculations constitute simulations of the heat transfer and chemical reaction trials performed in the experimental part of this investigation. The remaining calculations concern the illustration of approximate chemical similarity, the effect of distributed velocity and finite radial diffusivity on the parametric sensitivity found by Bilous and Amundson in a piston-flow model, programmed temperature control, and the thermal initiation of chemical reactions. The objects of the calculations and the sources of data are discussed in Chapter V.

Numerical Analysis

The numerical solution of the problem consisting of equations 106a through 107d is considered in this section. As mentioned in Chapter II, the solution of a boundary-value problem requires two steps. First, the derivatives in the original equations and boundary conditions are replaced by finite difference quotients to give a system of algebraic equations. Then values of the dependent variables are computed from these equations for a set of discrete points contained in the region of definition of the variables.

Reduction to a System of Ordinary Differential Equations.--The partial differential equations 106a and 106b and the boundary conditions 107b, 107c, and 107d are first approximated by a system of ordinary differential equations. The procedure was used by Hartree and Womersly (141) and has been developed extensively by Varga (142).

The solution to the problem is defined in the region $\bar{R}$: $0 \leq s \leq 1$, $0 \leq z \leq 1$. A set of points in $\bar{R}$ is determined by the intersection of the coordinate lines

$$s_i = ih_1 , \qquad i = 0,1,2, \ldots, I'$$

$$s_i = I'(h_1 - h_2) + ih_2 , \qquad i = I', I'+1, \ldots, I$$

$$z_n = n(\Delta z) , \qquad n = 0,1, \ldots, N$$

where $I'(h_1 - h_2) + Ih_2 = 1$ and $(\Delta z)N = 1$.

The functions, γ and θ, that satisfy equations 106a and 106b in $\bar{R}$ and boundary conditions 107a, 107b, 107c, and 107d are assumed to exist and have continuous third order derivatives with respect to s and z. The functions $\hat{u}$, $\hat{K}$, and $\hat{D}$ are seen to have continuous derivatives with respect to s through the second order. All of the quantities in equations 106c, 106d, and 106e are positive and non-zero in $\bar{R}$ with the exception of $\hat{u}$ and φ which are non-negative in $\bar{R}$ and vanish only for $s = 1$. The parameters P_1 and P_3 are positive constants. The parameter P_4 is a non-negative constant and P_2 is a constant that may be positive, negative, or zero. For the sake of brevity, the notation $W_{i,n} = W(s_i, z_n)$ is adopted.

For the purpose of numerical solution the boundary condition, 107a, may be approximated by

$$\theta_i = f_1(s_i) \quad \text{and} \quad \gamma_i = f_2(s_i) \tag{108}$$

The approximations used in the differential equations are shown below. Except for $i = I$, exactly the same approximations are used for both θ and γ, so only those for θ have been shown.

$i \neq 0, I', I$:

$$\left[\frac{1}{s}\frac{\partial}{\partial s}(s\hat{K}\frac{\partial\theta}{\partial s})\right]_i \doteq \frac{1}{s_i h^2}\left\{(s\hat{K})_{i-\frac{1}{2}}\theta_{i-1} - \left[(s\hat{K})_{i-\frac{1}{2}} + (s\hat{K})_{i+\frac{1}{2}}\right]\theta_i + (s\hat{K})_{i-\frac{1}{2}}\theta_{i+1}\right\}$$

$$\doteq a_{i,i-1}\,\theta_{i-1} + a_{i,i}\,\theta_i + a_{i,i+1}\,\theta_{i+1}\,. \tag{109a}$$

$i = 0$:

$$\left[\frac{1}{s}\frac{\partial}{\partial s}(s\hat{K}\frac{\partial\theta}{\partial s})\right]_0 = 2\hat{K}_0\left(\frac{\partial^2\theta}{\partial s^2}\right)_0.$$

Because of symmetry

$$2K_0\left(\frac{\partial^2\theta}{\partial s^2}\right)_0 \doteq \frac{4K_0}{h_1^2}(\theta_1 - \theta_0) = a_{0,0}\,\theta_0 + a_{0,1}\,\theta_1\,. \tag{109b}$$

$i = I'$:

$$\left[\frac{1}{s}\frac{\partial}{\partial s}(s\hat{K}\frac{\partial\theta}{\partial s})\right]_{I',n} \doteq \frac{2}{s_{I'}h_1h_2(h_1+h_2)}\left\{h_1(s\hat{K})_{I'-\frac{1}{2}}\theta_{I'-1}\right. \tag{109c}$$

$$\left. - \left[h_1(s\hat{K})_{I'-\frac{1}{2}} + h_2(s\hat{K})_{I'+\frac{1}{2}}\right]\theta_{I'} + h_2(s\hat{K})_{I'+\frac{1}{2}}\theta_{I'+1}\right\}$$

$$= a_{I',I'-1}\,\theta_{I'-1} + a_{I',I'}\,\theta_{I'} + a_{I',I'+1}\,\theta_{I'+1}$$

$i = I$: From 106d, 106e, and 107c

$$\left(\frac{\partial \hat{K}}{\partial s}\right)_I = \left(\frac{\partial \hat{D}}{\partial s}\right)_I = \left(\frac{\partial \gamma}{\partial s}\right)_I = 0 \quad \text{and} \quad s = 1 .$$

It follows that

$$\left[\frac{1}{s}\frac{\partial}{\partial s}\left(\hat{K}s\,\frac{\partial \theta}{\partial s}\right)\right]_I = \hat{K}_I\left[\frac{\partial^2 \theta}{\partial s^2} + \frac{\partial \theta}{\partial s}\right]_I .$$

Then, using the approximation,

$$\left(\frac{\partial^2 \theta}{\partial s^2}\right)_I \doteq \frac{2}{h_2^2}\left[\theta_{I-1} - \theta_I + h_2\left(\frac{\partial \theta}{\partial s}\right)_I\right] ,$$

$$\left[\frac{1}{s}\frac{\partial}{\partial s}\left(\hat{K}s\,\frac{\partial \theta}{\partial s}\right)\right]_I \doteq \frac{\hat{K}_I}{h_2^2}\left[2\theta_{I-1} - 2\theta_I + h_2(2 + h_2)\left(\frac{\partial \theta}{\partial s}\right)_I\right] .$$

On substituting for $\left(\frac{\partial \theta}{\partial s}\right)_I$ from 107d, this becomes

$$\left[\frac{1}{s}\frac{\partial}{\partial s}\left(\hat{K}s\,\frac{\partial \theta}{\partial s}\right)\right]_I \doteq \frac{\hat{K}_I}{h_2^2}\left\{2\theta_{I-1} - \left[2 + h_2(2 + h_2)A_x\right]\theta_I + h_2\,(2 + h_2)A_x\theta_j\right\}$$

$$= a_{I,I-1}\,\theta_{I-1} + a_{I,I}\,\theta_I + a_J\theta_J \qquad (109d)$$

Except for the boundary condition, the same approximation holds for γ at $i = I$, so

$$\left[\frac{1}{s}\frac{\partial}{\partial s}\left(\hat{K}s\,\frac{\partial \gamma}{\partial s}\right)\right]_I \doteq \frac{2\hat{D}_I}{h_2^2}\left(\gamma_{I-1} - \gamma_I\right)$$

$$= b_{I,I-1}\,\gamma_{I-1} + b_{I,I}\,\gamma_I \qquad (109e)$$

Two values of Δs, that is, h_1 and h_2, are used in the above approximations. From preliminary calculations it was known that third

and higher order derivatives of both γ and θ with respect to s would be small for $0 \leq s < 0.75$, but that some of these derivatives would become large for $0.75 < s \leq 1$. The errors of the s-approximations depend on the higher derivatives and are proportional to $(\Delta s)^2$. So, in order to reduce the error introduced by the s-approximations and to show more detail in the solution for $s > 0.75$, h_2 was chosen to be only one-fourth as large as h_1. The values used in these calculations were $h_1 = 0.1$, $h_2 = 0.025$, $I' = 7$, and $I = 20$.

The unsymmetric form of approximation 109c used at $i = I'$ might be expected to cause some erratic behavior in the computed values of θ and γ. On the other hand, serious difficulties were expected to be absent because the higher derivatives of θ and γ with respect to s were believed to be small for $s < 0.75$. Computing experience confirmed this belief and no noticeable instability or lack of smoothness was found in the solution at $i = I'$.

When the approximations 109 are substituted into equations 106, the following system of ordinary differential equations is obtained,

$$\hat{u}_o \left(\frac{\partial \theta}{\partial z}\right)_o = P_1 \left[a_{o,o}\, \theta_o + a_{o,1}\, \theta_1\right] - Q_1 R(\gamma_o, \theta_o)$$

$$\hat{u}_1 \left(\frac{\partial \theta}{\partial z}\right)_1 = P_1 \left[a_{1,o}\, \theta_o + a_{1,1}\, \theta_1 + a_{1,2}\, \theta_2\right] - Q_1 R(\gamma_o, \theta_1)$$

$$\vdots$$

$$\hat{u}_{I-1} \left(\frac{\partial \theta}{\partial z}\right)_{I-1} = P_1 \left[a_{I-1,I-2}\theta_{I-2} + a_{I-1,I-1}\theta_{I-1} + a_{I-1,I}\theta_I\right] - Q_1 R(\gamma_{I-1}\theta_{I-1})$$

$$0 = P_1[a_{I,I-1}\theta_{I-} + a_{I,I}\theta_I] + P_1 a_J \theta_J - Q_1 R(\gamma_I, \theta_I)$$

$$\hat{u}_o \left(\frac{\partial \gamma}{\partial z}\right)_o = P_2[b_{o,o}\,\gamma_o + b_{o,1}\,\gamma_1] - Q_2 R(\gamma_o, \theta_o)$$

$$\hat{u}_1 \left(\frac{\partial \gamma}{\partial z}\right)_1 = P_2[b_{1,o}\,\gamma_o + b_{1,}\,\gamma_1 + b\quad\gamma\,] + Q_2 R(\gamma_1, \theta_1)$$

$$\vdots$$

$$\hat{u}_{I-1} \left(\frac{\partial \gamma}{\partial z}\right)_{I-1} = P_2[b_{I-1,I-2}\gamma_{I-2} + b_{I-1,I-1}\,\gamma_{I-1} + b_{I-1,I}\gamma_I] + Q_2 R(\gamma_{I-1}, \theta_{I-1})$$

$$0 = P_2[b_{I,I-1}\gamma_{I-1} + b_{I,I}\,\gamma_I] + Q_2 R(\gamma_I, \theta_I) \quad (110)$$

If the $I + 1^{st}$ equation for both θ and γ are removed from this system, the remaining equations may be represented compactly in matrix notation,

$$\left(\frac{\vec{dV}}{dz}\right) = \left(\frac{\vec{P}}{u}\right) \cdot [A]\,\vec{V} + \left(\frac{\vec{Q}}{u}\right) \cdot \vec{R} + \left(\frac{\vec{P}}{u}\right) \cdot \vec{q} \quad (111)$$

$$P_1[a_{I,I-1}\,V_{2I-1} + a_{I,I}\,V_{2I}] = Q_1 R(\gamma_I, \theta_I) - P_1 a_J \theta_J$$

$$P_2[b_{I,I-1}\,V_{I-1} + b_{I,I}\,V_I\,] = -Q_2 R(\gamma_I, \theta_I) \quad (112)$$

$$V_{i+I}(0) = f_1(s_i), \quad V_i(0) = f_2(s_i) \quad (113)$$

where

$$[A] = \left[\begin{array}{c|c} b_{ij} & 0 \\ \hline 0 & a_{ij} \end{array}\right] \qquad \begin{array}{l} i = 0,1, \ldots, I-1 \\ j = 0,1, \ldots, I-1 \end{array}$$

$$\left(\frac{\vec{P}}{u}\right) = \left[\begin{array}{c} \frac{P_2}{u_i} \\ \hline \frac{P_1}{u_i} \end{array}\right] \qquad i = 0,1, \ldots, I-1$$

$$V = \left[\begin{array}{c} \gamma_i \\ \hline \theta_i \end{array}\right] \qquad i = 0,1, \ldots, I-1$$

$$\left(\frac{\vec{Q}}{u}\right) = \left[\begin{array}{c} \frac{Q_2}{u_i} \\ \hline \frac{Q_1}{u_i} \end{array}\right] \qquad i = 0,1, \ldots, I-1$$

$$\vec{q} = \left[\begin{array}{c} 0 \\ B_{I-1,I}\ \gamma_I \\ 0 \\ a_{I-1,I}\ \theta_I \end{array}\right]$$

$$\vec{R} = \left[\begin{array}{c} R(\gamma_i, \theta_i) \\ \hline R(\gamma_i, \theta_i) \end{array}\right] \qquad i = 0,1, \ldots, I-1$$

The dot notation, $\vec{W} \cdot [M] = [N]$, indicates a direct product, where the elements of the product matrix $[N]$ are given by

$$n_{ij} = W_i \, m_{ij}$$

In the case of two vectors, the dot notation signifies the inner product, as usual. In this system there are $2I$ ordinary differential equations, 2 algebraic equations, $2I + 2$ dependent variables and $2I + 2$ initial conditions, since f_1 and f_2 are known. Thus, there are neither too few nor too many relations and initial conditions to compute γ_i and θ_i as functions of z.

Reduction to a System of Difference Equations.--A wide variety of possible methods are available for solving the above system of differential equations. If the vector $\vec{q}$ were identically zero, analytical methods for solving systems of ordinary differential equations might be employed. Such methods are described, for example, in the book of Frazer, Duncan, and Collar (143). This vector will be zero only in trivial cases, however. If R is linear, equations 112 may be solved explicitly for γ_I and θ_I; otherwise approximate solutions may be obtained by Newton's method. Any of the numerical methods suitable for the solution of systems of ordinary differential equations may be considered as methods for the system 111.

The errors of approximation in the s-direction have not been shown in equations 111, but these may be obtained from the Taylor series remainders corresponding to approximations 109. The size of the coefficients of the error terms may be controlled by I, that is, by the

number of equations in the system. For a given computer with a fixed information storage capacity, the permissible maximum value of I will depend on the method of solution. The magnitude of the errors that result from the approximation of $(\frac{d\vec{V}}{dz})$ in the system 111 depends on the approximation and on the choice of Δz. Thus, the magnitude of the error is dependent on the choice of the method used for the solution of the system, the allowable computing time, the value of I, and the size of Δz.

The method used for the solution of system 111 is based on the backward difference approximation for the first derivative,

$$\frac{W_n - W_{n-1}}{\Delta x} \doteq \left(\frac{dW}{dx}\right)_n$$

This method was chosen because of its simplicity and stability. Other methods which could have been used are those of Crank and Nicolson (99), Runge and Kutta, and Hamming (144). When the backward difference approximation is used, equations 111 become

$$[B]\,\vec{V}_{n+1} = \vec{V}_n + (\Delta z)\,(\underline{\vec{Q}}_u) \cdot \vec{R}_{n+1} + (\Delta z)(\underline{\vec{P}}_u) \cdot \vec{q}_{n+1} \qquad (114)$$

where $[B] = [I] - (\Delta z)(\underline{\vec{P}}_u) \cdot [A]$ and $[I]$ is the unit matrix.

Method of Computation.--Starting from the initial vector, given by equations 113, the vectors $\vec{V}_n$ are computed for $n = 1, 2, \ldots N$ in a step-by-step process. Since $R(\theta, \gamma)$ is not linear in general, equations 114 and 112 must be solved by an iterative procedure. The vector $\vec{V}_n$ and

the values of $V_{I,n}$, $V_{2I,n}$, and $\theta_{J,n}$, and $\theta_{J,n+1}$ are considered known. A first estimate of $\vec{V}_{n+1}$ is obtained from the forward difference analog of equation 114,

$$\vec{V}_{n+1} = [C]\, V_n + (\Delta z)\left(\frac{\vec{Q}}{u}\right) \cdot \vec{R}_n + (\Delta z)\left(\frac{\vec{P}}{u}\right) \cdot \vec{q}_n \qquad (115)$$

where $[C] = [I] + (\Delta z)\left(\frac{\vec{P}}{u}\right) \cdot [A]$.

This computed $\vec{V}_{n+1}$ is used to give first estimates of $\vec{R}_{n+1}$ and $\vec{q}_{n+1}$. These are used to improve the vector $\vec{V}_{n+1}$ by equation 114. For $\vec{R}_{n+1}$ and $\vec{q}_{n+1}$ considered known, 114 can be solved readily by elimination, since $[B]$ is tri-diagonal. The details of the elimination process may be found in the book of Forsythe (145). The improved $\vec{V}_{n+1}$ is again used to compute $\vec{R}_{n+1}$ and $\vec{q}_{n+1}$, and these are again substituted into 114 to give a new set of values for the elements of $\vec{V}_{n+1}$. This process is continued until the changes in each of the elements of the vector $\vec{V}_{n+1}$ are all less than some predetermined value.

Between the completion of the n^{th} step and the beginning of the $(n + 1)^{st}$ step, the jacket temperature is changed by an increment which may be positive, negative, or zero. That is, $\theta_{J,n+1} = \theta_{J,n} + \Delta_J$. The value of these increments and the value of z where they become effective are included in the data for the computer. For example, see Table 9.

The program actually used for computation appears in Appendix II. It is written in the Burroughs version of ALGOL 58, the International Algorithmic Language. The computer employed for the calculations was

a Burroughs 220 machine with a 5,000-word memory and auxiliary magnetic tape storage units.

Validity of Solutions.--Equations 112, 113, and 114 represent a formal approximation to the original differential equations and boundary conditions. However, the fact that a system of difference equations is a formal approximation does not guarantee that the solution to the system will be close to the solution of the original boundary value problem. In some cases the desired proofs have been carried out, but none of them are directly applicable to the problem of this thesis.

Three questions are involved. First, there is the question of stability: Does the cumulative error for a given point in $\bar{R}$ grow faster than some power of $(\Delta s)^{-1}$ or $(\Delta z)^{-1}$ as Δs and Δz tend to zero? Second, there is the question of convergence: Does the departure of the solution of the approximate problem from the solution of the original boundary-value problem tend to zero as Δs and Δz approach zero? Finally, since only a finite number of digits can be handled by a real computer, the solution of even the approximate boundary-value problem cannot be exact. So one also has the question: Are the errors due to rounding-off of excess digits tolerable?

The question of stability is difficult to answer for problems as complicated as the present one. The non-linearity of $R(\gamma, \theta)$ prevents the use of Fourier methods or the matrix methods of Douglas (126) in an investigation of this question. The best that can be done in this direction is to assume that the behavior of the system is similar to that of simpler systems. For example, Richtmeyer (146) considers the problem

$$\frac{\partial \gamma}{\partial t} = \sigma \frac{\partial^2 \gamma}{\partial x^2} + a \frac{\partial \gamma}{\partial x} + b\gamma \qquad (116)$$

where σ, a, and b are constants and $\sigma > 0$. He gives two examples and states that, "They (and others) support the conclusion that for diffusion problems, at least, stability is practically unaffected by the lower order terms." Thus, a method which is unconditionally stable for

$$\frac{\partial \gamma}{\partial t} = \sigma \frac{\partial^2 \gamma}{\partial x^2} , \quad \sigma > 0$$

is expected to be stable for 116. Fortunately, instability is easily recognized by an inspection of numerical results. The numbers produced from an unstable system of difference equations will either grow extremely rapidly or oscillate wildly. Also, it is known that in some cases, for a fixed Δs, there is a critical value of Δz below which stable behavior occurs. So, if unstable behavior were encountered in solving system 114, the trouble might be solved by reducing Δz.

The question of convergence has been attacked for a number of boundary-value problems that include non-linear partial differential equations. The investigations most nearly applicable to the present problem are those of Lees (183) and Rose (182), mentioned in Chapter II. An attempt to apply Lees' work to the problem of this investigation indicated that results analogous to his could be obtained for a system

of partial differential equations. Unfortunately, equations 106 and boundary conditions 107 do not fulfill the hypotheses of Lees' theorem. There are at least three unsatisfied hypotheses. First of all, Lees has a zero error on the boundaries $z = 0$, $s = 0$, and $s = 1$, but in the present problem the error vanishes only on $z = 0$. Second, $\hat{u}$ is not bounded away from zero in $\bar{R}$ as required by the theorem. Finally, $\hat{K}$ and $\hat{D}$ are only twice "boundedly differentiable" in $\bar{R}$ instead of the three times called for by Lees. The lack of satisfaction of the last two hypotheses is encountered also with the weaker theorem of Rose.

The question of accumulated round-off error is not serious for the solution of 114 by the method described above. This can be seen from the computations in which $f_1(s)$ is constant, $Q_1 = 0$, and $a_J = 0$. In these θ should be constant with respect to both s and z throughout $\bar{R}$. The same sort of test can be made also for γ. In practice, the average round-off errors were found to be about 2×10^{-4} per cent per step for θ and 2×10^{-5} per cent per step for γ.

Beyond questions of the mathematical validity of the numerical solutions, there is no <u>a priori</u> assurance that the mathematical model used here is capable of describing chemical reaction, heat transfer, and diffusion in a tubular reactor. The best that can be done under the present circumstances is to compare the numerical solutions with experimental data. A good agreement between the two, although it is no proof, could certainly be considered as evidence supporting the

validity of both the mathematical model and the method of numerical analysis.

CHAPTER IV

EXPERIMENTAL INVESTIGATION

Objectives of This Investigation

An experimental investigation of a jacketed tubular reactor was undertaken to provide data for comparison with theoretical results and to test some of the assumptions on which theoretical formulation of the problem was based. In order to obtain a convincing test of the assumptions, it was considered necessary to secure local values of velocity, temperature, and concentration, as well as bulk values. The reason for this is that the bulk average of some variable, W, of a fluid flowing in a steady state past a cross section of a pipe is given by

$$\overline{W} = \frac{2\int_0^{r_w} u(r)\, w(r)\, r\,dr}{r_w^2\, \overline{u}} \tag{117}$$

An experimental determination of $\overline{W}$ does not determine W as a function of r, even when $u(r)$ is known. From another point of view, it is possible for a method of computation that has $W(r)$ as its primary results to give a bulk average $\overline{W}$, which agrees with experiment, yet gives a $W(r)$ which does not agree with the values of W determined by experiment for particular values of r. Accordingly, it is necessary to know local experimental values of W in order to test a theoretical calculation which gives $W(r)$ as its primary result.

The theoretical calculations corresponding to the data obtained with the jacketed, tubular reactor were based on velocity and eddy-diffusivity profiles, kinetic data, physical properties of the reaction mixture, and assumptions concerning the effect of temperature gradients on the velocity and eddy-diffusivity profiles. Obviously, errors in these bases may affect the theoretical results so that a comparison of experiment and theory may not be a completely valid test of the method of calculation. An effort was made to supply enough basic data to remove most of the ambiguity in a comparison of calculated and experimental results.

Boundary Conditions

As mentioned in Chapter III, the conflicting needs for a practical method of initiating the reaction and for an accurate mathematical description were reconciled in this investigation by mixing the reactants and allowing the velocity profile of the reaction mixture to develop upstream from some cross section that is considered to define the reactor inlet. Thus, at the reactor inlet, the experimentally measured velocity, temperature and concentration profiles have been taken as the boundary conditions. This should be satisfactory for reactors in which little reaction occurs during the mixing of the reactants and most of the reaction is induced at a later stage, by heat or light. It would leave something to be desired when there is appreciable reaction during the mixing of the reactants. The most realistic approach to such problems seems to be to use the autoclave-series analogy for the entrance section of the tube and thus estimate

the concentration and temperature for some cross section where the velocity profile may be considered as fully developed.

Description of Equipment

General Plan.--The reaction used in this investigation was the saponification of methyl acetate with sodium hydroxide. A flow diagram of the apparatus is shown in Figure 1. The reactants, aqueous sodium hydroxide and methanolic methyl acetate, were pumped by small centrifugal pumps from drums to the reactor area via calibrated rotameters. The water used as diluent in the reaction mixture was taken from a constant head tank, supplied from the water main through a float valve. This water was pumped through a 50-micron filter and a calibrated rotameter and then was split into two streams, approximately equal in size. The concentrated reactants were mixed with these two water streams and the diluted reactant streams then entered the mixing section at the bottom of the reactor. The resulting reacting mixture flowed vertically through the reactor to the top, then the partially reacted mixture flowed by gravity down a waste pipe into a weighing drum on portable scales and thence to the sewer.

The main piece of equipment was a vertical, jacketed, tubular reactor divided into five jacketed sections. The jackets of the lowest section and the second section, that is, the mixing and profile development sections, were supplied with circulating cold water from the constant head tank. The jackets of the remaining three jacketed sections were connected in parallel to a circulating hot water

system. When this system was used, the water was heated by steam in a small shell-and-tube heat exchanger. The temperature of the water leaving the exchanger was held constant by a self-actuating temperature controller.

Three two-inch sections of the reactor were fitted with probes for measuring impact pressure and temperature and for withdrawing samples. Each sample line was designed so that it could be refrigerated with cold acetone, if desired. It was also possible, when desired, to connect a sample receiving flask to a regulated vacuum system. Impact and static pressures were transmitted to a manometer at the first level by means of copper tubing. The voltages of the fifteen thermocouples in the reactor assembly were transmitted by wire to a potentiometer located at the first level.

Reactor.--The arrangement of the reactor is shown in Figure 1. It was nineteen feet tall and consisted of five jacketed sections, three test sections, each two inches high, and one unjacketed end section 2-1/2 feet in height. The jacketed sections were one, four, four, three, and four feet in height, respectively (in order from bottom to top). The reactor was made from one-inch, schedule-80 pipe and jackets from two-inch, schedule-40 pipe. The reactor tube and flanges were type-304 stainless steel, the jackets were aluminum, and the overflow box at the top of the reactor was made of plywood painted with two coats of epoxy resin. Other materials used in the construction of the reactor were various epoxy resins reinforced with glass fabric or glass fibers, copper tubing for the reactor-inlet and static-pressure

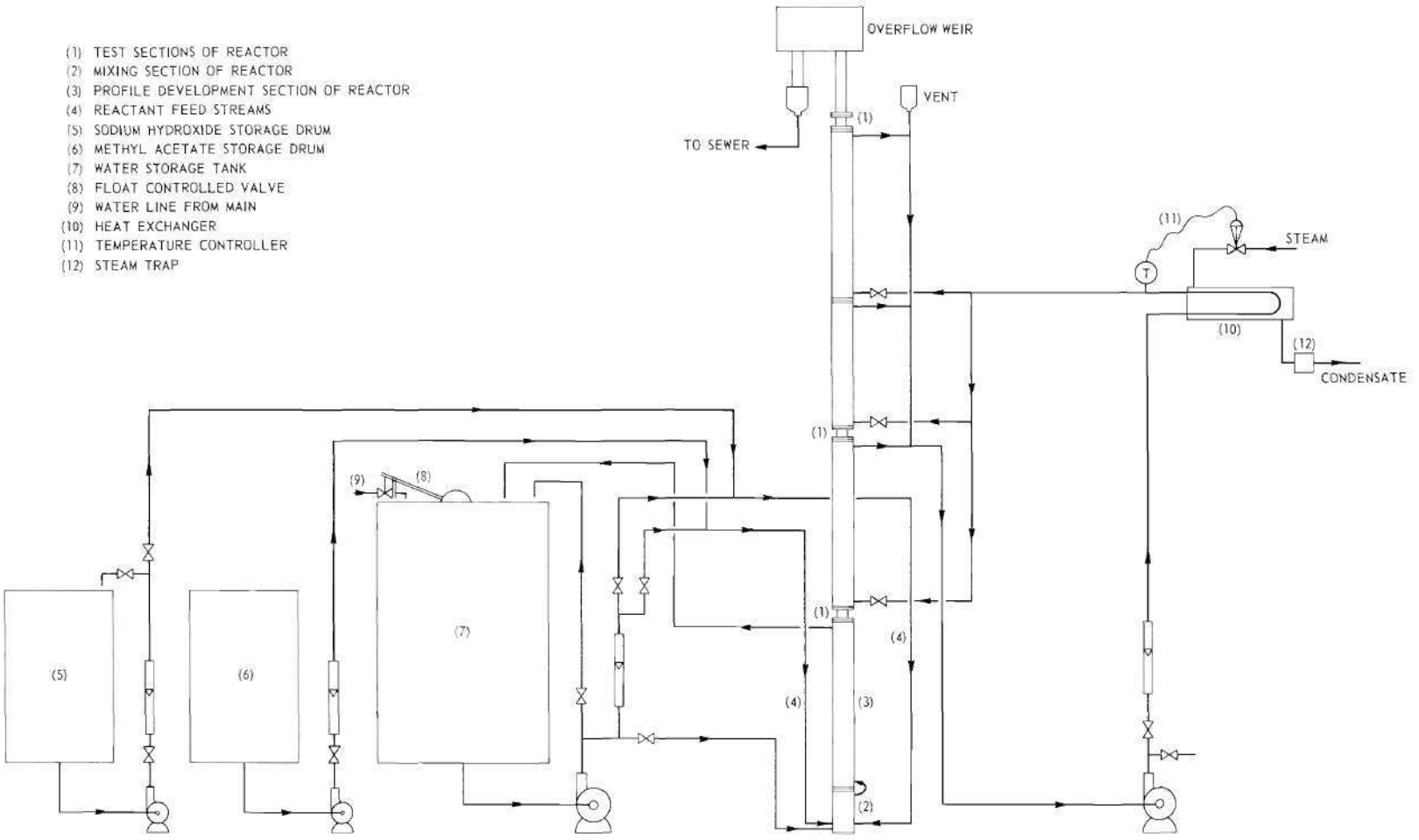

Figure 1. Flow Diagram.

connections, stainless-steel and nickel-alloy tubing for the impact-pressure and sample probes, and Buna-N rubber O rings for the seals between the flanges of the reactor sections and for the probe shaft seals in the test sections.

The interior surface of the reactor tube was rough when received and somewhat deformed from the shape of a true cylinder. There was an eccentricity in the shape of the cross section, such that the axis of the eccentricity described a spiral about the axis of the tube. Most of the roughness and a large part of the eccentricity were removed by repeated honing with a piston-pin hone. The diameter before honing was 0.955 ± 0.006 inch. After honing, it was 0.960 ± 0.003 inch. Pressure-drop measurements after honing gave friction factors which corresponded to a relative roughness, ε/r_w, of approximately 0.00065.

The flanges for the reactor sections were four inches in diameter and 1/4 inch thick. Shoulders were turned on the ends of each of the reactor sections; the flanges were forced onto these shoulders and bonded to the tube sections with an aluminum-filled epoxy resin, reinforced with several layers of glass fabric. Each flange was then faced on a lathe, and a groove for a O ring two inches in diameter was cut in the face of each of the top flanges. Reactor sections were joined by bolting together the adjacent flanges. When the sections were joined, the O ring was compressed to form a seal at the flanged joint. The use of an O ring seal instead of a conventional gasket permitted the flanges to be brought together more closely, that is, with a smaller crack at the inner surface of the tube. Adjacent sections were alined by visual and tactile inspection; then holes

were drilled and reamed in the joining flanges, which were pinned to maintain the alinement.

The aluminum pipe for the jackets was first cut into sections to fit the flanged sections of the reactor tube. Then each of the sections of aluminum pipe was sawed lengthwise into halves and fitted to its corresponding reactor section. One of the halves was drilled and tapped to permit two one-inch pipe nipples to be attached at the top and bottom of the jacket. The jacket halves were attached to the tube flanges by epoxy resin, reinforced with glass fabric, and the slits in the jacket sides were sealed with resin-fabric laminate. The jackets were tested at an air pressure of eight pounds per square inch, and all leaks were sealed before the jackets were placed in service.

The first, short section of the reactor was used to mix the reactant streams. Four off-center holes, two for each reactant stream, were milled in the tube wall of this section so that the entering streams would create a swirling flow pattern. Copper tubing connections, 3/8 inch in diameter, were inserted in the holes and joined to the tube wall with epoxy resin. In order to remove the swirling flow pattern, a set of straightening vanes, four inches long, was made from four interlocking rectangles of sheet iron. The vanes were fitted together, ground down to fit the reactor tube, bonded together with resin, and finally coated with resin to prevent corrosion. This set of vanes fitted in the reactor tube very tightly, but to be sure that the vanes did not fall and interfere with the mixing action in the

bottom portion of this section, a thin brass ring was bonded to the inside of the tube wall, four inches from the top of the section.

Test Sections.--Each of the reactor test sections consisted of a short spool of pipe, two probe assemblies, and traversing mechanisms for the probes. These test sections were at levels of five, ten, and eighteen feet above ground level. A photograph of one of these sections is shown in Figure 3. Each section was two inches tall, and the flanges were attached to the ends as described above. One inch above the face of the bottom flange, two holes were drilled in the tube wall, normal to it and so that their common center line coincided with a diameter of the reactor section. Seals that permitted the probe shafts to be moved back and forth through the wall of the reactor were positioned in these holes and bonded to the reactor tube with epoxy resin. Grooves were cut in the inner surface of the reactor wall between these holes and the bottom flange face. The grooves were square and sufficiently wide and deep so that the probes could be retracted into them.

The probes were attached to shafts of nickel-alloy tubing, each of which had an outside diameter of 1/8 inch, a wall thickness of 0.010 inch and a length of 2-3/4 inches. An impact-pressure probe consisted simply of a one-inch length of 20-gage, stainless-steel, hypodermic-needle tubing, the end of which was rounded to approximate the surface of a spherical sector. This was attached to its shaft in the following manner. The end of the shaft was plugged with epoxy resin, reinforced with glass fibers. A 0.035-inch hole was drilled through the plug along the axis of the shaft and another hole for the

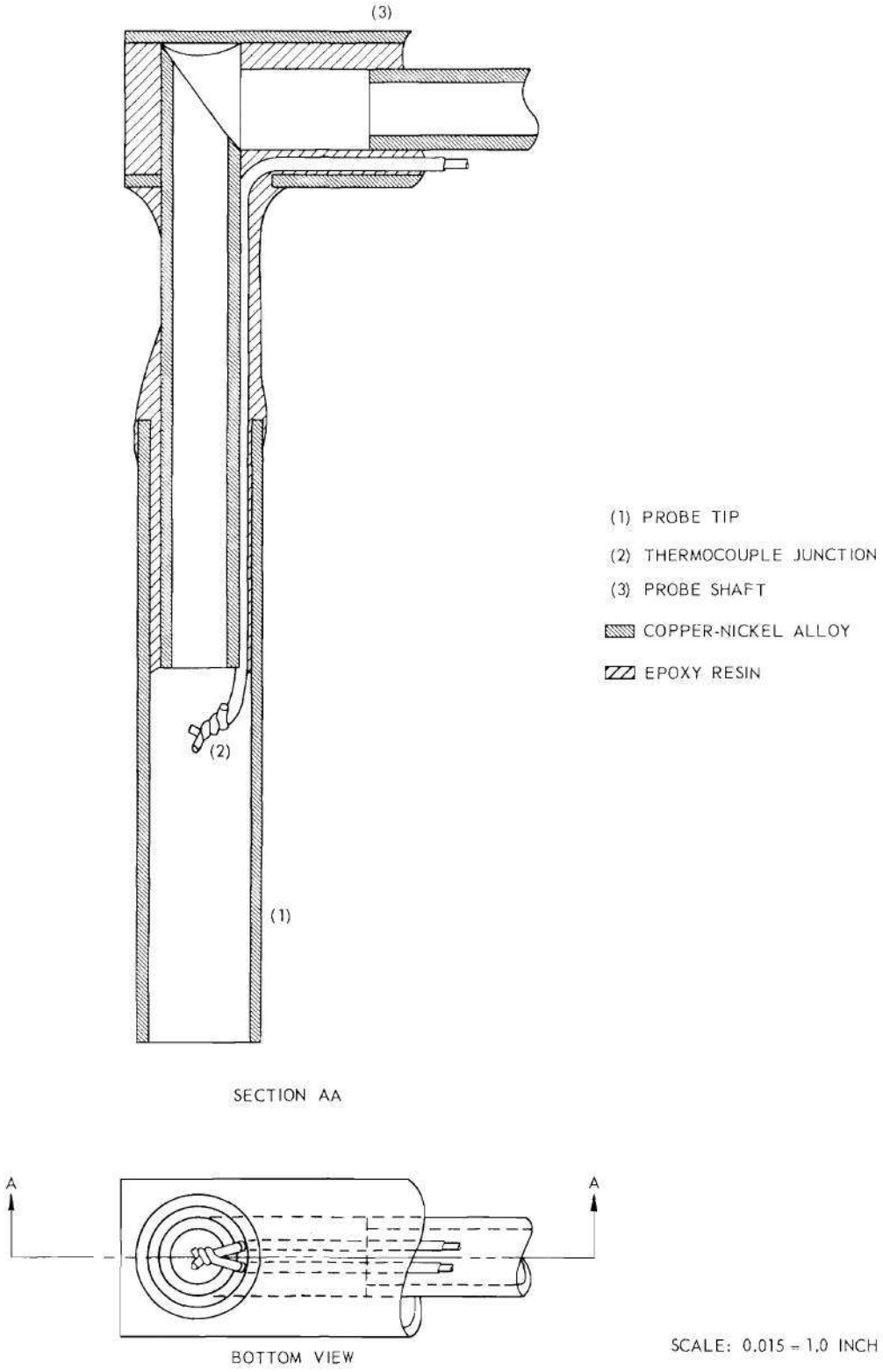

Figure 2. Details of Sampling Probe.

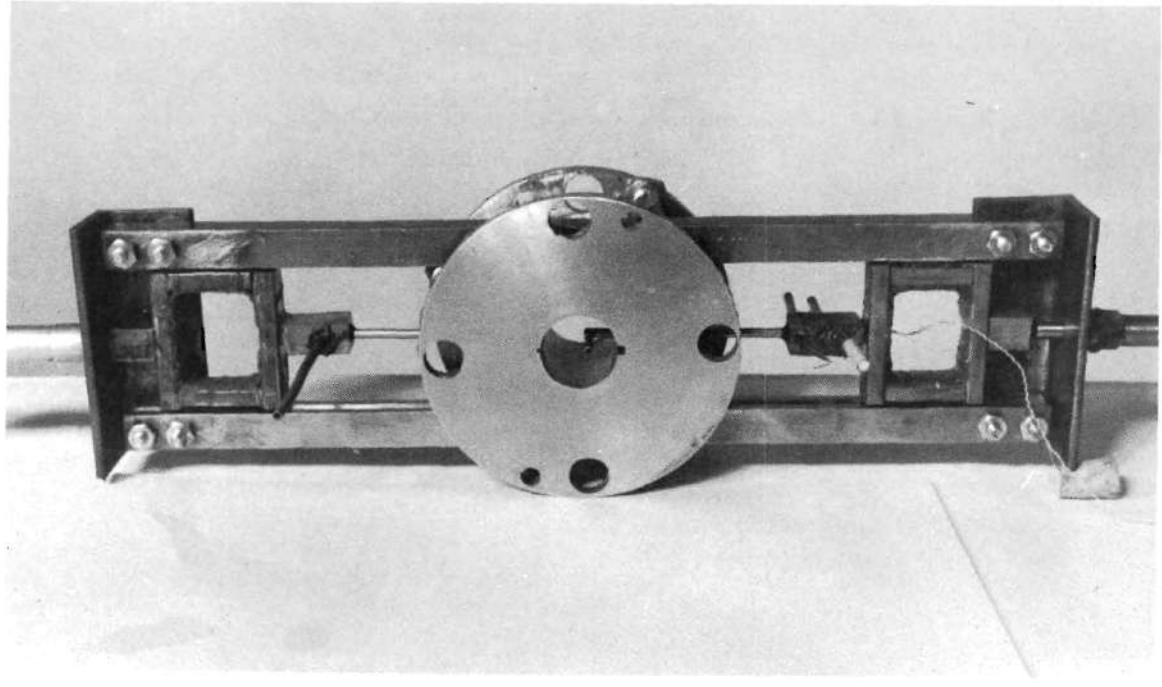

Figure 3. Bottom View of Typical Test Section.

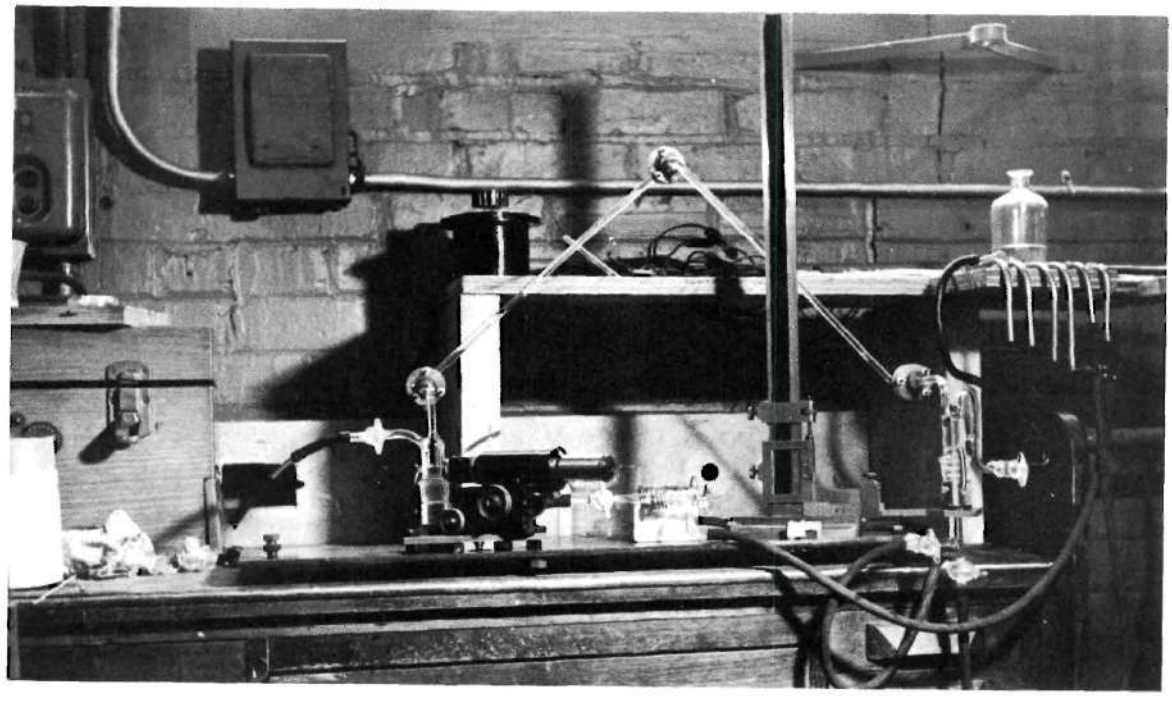

Figure 4. Front View of Manometer.

probe was drilled near the end of the shaft, normal to the axis of the shaft and intersecting the first hole. When the impact-pressure probe was inserted into the shaft, it was mechanically supported by the plug of epoxy resin inside. Additional resin was used to seal the probe to the shaft and to fill the hole at the end of the shaft. This method permitted a relatively strong joint between the stainless-steel probe and the nickel-alloy tubing to be made with epoxy resin.

The sampling probes, which also contained thermocouple junctions, were more complicated than the impact-pressure probes. The probe assembly was designed to permit the sample stream to be cooled as soon as it entered the probe shaft. Unfortunately, after a few hours of operation, the coolant passages in the probe shaft became plugged with rust and dirt from the coolant circulation system so that this feature of the apparatus could not be used. The details of a sampling-probe assembly are shown in Figure 2. The probe itself was made from two pieces of nickel-alloy tubing which had outside diameters of 0.062 inch and 0.100 inch, respectively, and had wall thicknesses of 0.010 inch. The larger tube was the probe tip and contained a thermocouple junction, the wires of which passed between the two tubes where they were bonded together. Each of these probes was attached to its shaft in a manner similar to that used for the impact-pressure probes except that a brass support plug was used in one instance. The shaft of a sampling probe contained three passages, one for the sample stream and one each for the coolant stream flowing in and out. In addition, the wires from the thermocouple junction were run through the passage for the outgoing coolant. Each probe shaft was attached to a connection block machined from a

cast block of epoxy resin. Short connections of metal tubing for the coolant and sample streams were bonded to one side of the connection block, and a thermocouple junction was inserted in the sample stream at the end of the block.

The connection blocks for the sampling probes and the impact-pressure probes were attached themselves to probe carriages. These were simply rectangles formed from short pieces of steel-bar stock bonded together with epoxy resin and had two bearing balls, 1/8 inch in diameter, bonded with resin to the outside of each of the short sides of the rectangle. These bearing balls enabled the probe carriage to slide in guides consisting of two lengths of square, steel-bar stock, each of which had a V groove cut lengthwise in the middle of one side. The guides were clamped to the bottom flange of the test section, and the ends of the guides on either side of the test section were bolted to pieces of angle iron which served as micrometer head supports and helped to hold the guides parallel to one another. Micrometer heads graduated in thousandths of an inch were bonded to the outside of the micrometer head supports. Each of the supports had a hole for the micrometer spindle which contacted a bearing ball bonded onto the rear side of the probe carriage. Since a probe, probe shaft, connection block, and probe carriage were rigidly connected, the displacement of a probe in the reactor could be determined by measuring the displacement of its probe carriage with a micrometer. Before the test sections were installed, micrometer readings were recorded for each probe when fully retracted and when centered at the radius of the tube wall. These

readings enabled the positions of the probes to be determined relative to the tube wall.

The static pressure corresponding to the impact pressure at a given test section was not measured at the test section but at holes in the reactor wall located one inch upstream from the tip of the impact-pressure probe, that is, one inch below the corresponding test section. Two holes, 1/32 inch in diameter, were drilled on a diameter of the reactor cross section. Copper tubes were connected to these holes at the reactor wall, passed through holes in the jacket wall, and joined together outside the reactor.

Manometer.--Small differential pressures were measured in a liquid under relatively large static pressure. The manometer used for these measurements was especially designed for this situation. The characteristics desired were freedom from capillary effects, accuracy, rapidity of response, minimum fluid displacement in the pressure transmission lines, a large range, and a minimum cost.

The use of impact pressure measurements for the determination of local velocities in a flowing fluid has led to the design of many sensitive manometers. For a description of some of the better known designs, the reader is referred to the books of Ower (147) and Prandtl and Tietjens (148). After a number of different models were built, tested and found to be unsatisfactory, a manometer was built that was similar, in principle, to those of Chattock (149) and Douglas (150), except that it was completely liquid filled, including the transmission lines. This manometer, as it was used, was sensitive to ± 0.0002 inch

of water under favorable conditions, that is, steady pressure differences and short transmission lines. The sensitivity of the manometer could have been improved upon easily, but this was not warranted since fluctuations in the observed impact pressure would not have allowed any improvement in accuracy. The range of the manometer as used was about 3.2 inches of water; this could have been increased through the use of a longer scale having sufficient accuracy.

The manometer was essentially an inverted U tube, the legs of which were connected to the pressure transmission lines. A photograph of this instrument is shown in Figure 4. The manometer consisted of two glass reservoirs; a connection between them that was made from glass tubing and swivelling, ball-and-socket joints; a height gage; and a microscope. The left-hand reservoir, the microscope and the height gage were fixed to a steel plate, 1/2 inch thick. The right-hand reservoir was carried by the movable part of the height gage and so could be moved in the vertical direction. The connecting pieces of glass tubing and the top portions of both reservoirs were filled with kerosene; the bottom portions of the reservoirs and the transmission lines connected to the latter were filled with water. In the left reservoir, a bubble of kerosene projected into the water layer. When the manometer was balanced, the right reservoir was positioned so that the bottom of the bubble in the left reservoir would appear in the cross hairs of the microscope. The ratio of the cross sectional area of the right reservoir to that of the bubble tube in the left reservoir was 13. The microscope used to view this bubble had a magnification ratio of about 22.5. The

height gage had an 18 inch scale and could be read to 0.001 inch by means of a Vernier scale. The density of the kerosene was measured pycnometrically, and the difference in the densities of the kerosene and water was 0.1829 gram per cubic centimeter at 21.8°C and 0.1872 gram per cubic centimeter at 31.4°C.

One unusual problem encountered with this manometer was the need for a kerosene-insoluble "grease" to lubricate and seal the ball-and-socket joints. The following formula was found to be satisfactory:

Anhydrous glycerol	20 grams
"Carbowax 4000" (polyoxyetheylene glycol)	10 grams
Triethylene glycol	2 grams
Soluble starch (made by heating starch and glycerine)	5 grams

Triethylene glycol and "Carbowax" were added to the glycerol and heated until the "Carbowax" was completely melted. The powdered soluble starch was then added and dispersed and the resulting mixture heated to 140°C. The mixture was then cooled with constant stirring. A similar formula, without any soluble starch, was used as "grease" in the stop-cocks exposed to kerosene.

Sampling Apparatus.--The apparatus used to take samples from the reactor was designed to minimize the increase in the extent of reaction in the sample stream. This was done in two ways, by reducing the mean residence time of the sample stream in the sampling line and by cooling the sample stream. The samples were withdrawn through a sampling line

that consisted of lengths of nickel alloy tubing joined by silicone rubber tubing. The line was connected to one arm of a three-way stopcock. Of the two remaining arms of the stopcock, the upper one was connected by silicone rubber tubing to a burette. The lower arm of this stopcock extended about an inch into the receiving flask, and the sample stream fell directly from the tip of this lower arm into the dilute acid solution in the flask. Samples were sometimes withdrawn from the reactor under reduced pressure; in these circumstances, filtering flasks were used to receive the samples, and both the flasks and the burette were connected to a vacuum line.

Obviously, if the volumetric flow rate of the sample stream exceeded the local flow rate in the reactor at the location of the sample probe, fluid would be drawn into the probe tip from the region surrounding the probe. This condition would introduce uncertainty into the determination of the local average concentration and temperature. To avoid uncertainty from this source, the sample flow rate at the probe tip must be made less than that flow rate which would be intercepted by the area of the probe tip if the flow were undisturbed. Thus, for a given tip size and local flow rate, the sampling rate must be less than some maximum value. However, the mean residence time in the sample tube is not entirely controlled by the sampling rate at the probe tip. If the cross-sectional area of the tube connecting the probe tip with the sample receiving flask is less than the area of the tip, the mean residence time will be less than if they had the same area. It is advantageous to have a small-diameter sampling line,

but here again there is a limitation. For a given probe size the lower limit of the size of the sampling line, and thus of the mean residence time, will be controlled by the length of tubing, the pressure difference available for forcing the sample to flow from the reactor, and the maximum of the desired sample flow rates. The available pressure difference was comprised of the static pressure of the fluid column in the reactor, the difference between atmospheric pressure and that of a regulated vacuum system, and the impact pressure of the fluid. For the removal of samples from the top test section, where the static pressure was relatively small, vacuum was always used. The use of vacuum for sampling at the other two test sections depended on whether it was needed to obtain the desired sample flow rate.

A sampling-probe tip had a circular cross section with an inside diameter of 0.080 inch. The inside diameter of the connecting line was 0.042 inch. The silicone rubber tubing used in the line was cast from Dow Corning "Dilastic RTV 521" and had an outside diameter of 1/4 inch. A silicone rubber adapter which fitted the glass capillary tubing of the stopcock was made together with a piece of rubber tubing as a unit.

Cooling of the sample stream was supposed to be accomplished partly inside the probe shaft and partly in a sample cooler placed in the sampling line. As mentioned above, the coolant passages in the probe shaft quickly became plugged with rust and dirt, so that all of the cooling was done by the sample cooler. This device was a miniature

double tube heat exchanger, the inner tube of which was a five-inch length of the nickel-alloy tubing used in the sample line and the outer tube a piece of glass tubing 3/4 inch in diameter. Cold acetone at temperatures from - 18°C to - 12°C circulated through the outer tube.

Control of the sample flow rate was accomplished by adjusting a pinch clamp on one of the silicone rubber sections of the sample line. Measurement of the sample flow rate was done in two ways. In one, the flow rate was measured by timing the rising level in the burette connected to the three-way stopcock. In the other method, the flow rate was obtained by measuring sample weights and sample times.

Temperature Measuring Apparatus.--All temperature measurements were made with soft-soldered, copper-Constantan, thermocouple junctions. These thermocouples were individually calibrated before use against an accurate thermometer graduated in divisions of 0.1°C. The differences between the potentials of the fifteen thermocouples at the same temperature were less than 0.01 millivolt at calibration temperatures from 5°C to 60°C. These differences in potential appeared to be caused mainly by variations in the temperature of the thermostatting bath during calibration. Since the differences between the thermocouples were so small, the potentials at each calibration temperature were averaged to give a mean calibration curve, which was used for all of the couples. The calibrations and the subsequent measurements of temperature during the investigation were made with a Leeds and Northrup Portable Precision Potentiometer having an accuracy of ± 0.01 millivolt.

Miscellaneous Equipment.--During the tests in which heat was to be transferred to the reactor tube, hot water was circulated through the jackets of the third, fourth, and fifth reactor sections connected in parallel. The hot water system consisted of a 25-gallon-per-minute centrifugal pump; a four-pass, steam-heated, shell-and-tube heat exchanger for heating the water; a Fulton "Sylphon" self-actuating temperature regulator for controlling the water temperature; and connecting pipe. The jacket fluid temperatures were measured by means of thermocouple junctions placed in the inlet and outlet of each jacket.

A Podbielniak "Flokold" coolant supply was used to furnish cold acetone to the sample coolers, and a mechanical vacuum pump was used to obtain the reduced pressure in the vacuum system. The pressure in this system was held steady at an absolute pressure of about ten inches of mercury by a Conoflow vacuum regulator.

Non-Metallic Materials.--Epoxy resins of various types were used extensively in constructing the equipment used in this investigation. The characteristics which make these resins useful for such service are resistance to corrosion and solvent attack, a high ratio of strength to weight, relatively high working temperatures for certain resin-hardener combinations, and good adhesion to metals. Not only were these resins used for metal-to-metal bonds, but also small parts were made from them by casting or by casting and machining.

Several comments can be made on the basis of the experience with epoxy resins in this work. First of all, the substitution of small parts of epoxy resin for small metal parts is not advantageous unless

there are many such parts to be made or unless the machining or forming operations are difficult to perform, either due to the properties of the metal or to the peculiarities of the desired shape. The time consumed in pattern and mold preparation and curing the resin can be substantially more than machining time for equivalent metal parts. If it should be desirable to cast small parts using epoxy resin, some time and effort may be saved by making molds from a silicone rubber that vulcanizes at room temperature. Epoxy resins proved to be very useful in bonding various surfaces together; but if the joint design is poor, or if the surface preparation is not carefully done, the results will be poor. The resins or resin-hardener systems used in this work are listed in Table 4.

Table 4. Epoxy Resins Used in Construction of Equipment

Item	Name of Resin and Hardener	Manufacturer
1	Resiweld 105	H. B. Fuller Company
2	Resiweld 600	H. B. Fuller Company
3	617C	The Marblette Corporation
4	Epon 825*	Shell Chemical Company
5	Bakelite ERL 2795*	Union Carbide Plastics Company

*These were used with the following hardeners: diethylene triamine, Bakelite ZZL0814, meta-phenylene diamine.

Reactants

The reactants used in this investigation were sodium hydroxide, purchased as a 50 weight per cent aqueous solution, and methyl acetate, purchased as a 50 to 58 per cent solution in methanol. A typical analysis of the latter was as follows:

Ester content as methyl acetate	56.4 per cent by weight
Acidity as acetic acid	0.027 per cent by weight
Specific gravity at 76°F	0.867

In addition, a gas chromatographic analysis was made to detect the presence of constituents other than methanol and methyl acetate. No other compoenets were found with concentrations larger than about 0.5 per cent.

Procedure

General Description.--Five kinds of tests were made using the reactor tube. First of all, isothermal flow tests aere performed to obtain velocity and friction factor data. Then, temperature and velocity profiles were determined for heat transfer tests. Temperature and concentration data were obtained in chemical reaction tests performed with very small rates of heat transfer. There was no circulation of water through the reactor jackets and the temperature of the water in the jackets was the same as that of the ambient air. The term "pseudo-adiabatic" has been applied to these tests because the reactor tube was not actually insulated while they were being performed. Temperature and concentration data were also obtained in chemical reaction tests performed with appreciable rates of heat transfer. Finally, velocity data were obtained in a pseudo-adiabatic chemical reaction test.

Isothermal Velocity Profiles.--The procedure for measuring isothermal velocity profiles was quite simple. The constant-head tank was emptied and refilled before each test so that the temperature of the water pumped to the tube at the start of the test would be substantially the same as the temperature of the water in the main. The transmission lines for

conducting impact and static pressures to the manometer were filled with water. This had to be done very carefully so as to exclude air bubbles from the transmission lines. The volumetric flow rate was measured several times during a test by measuring the time required to collect a given mass of effluent in a weighing drum on portable scales. In addition, the flow rate was indicated by a rotameter, which was read at frequent intervals to insure that the flow rate remained constant. For the purpose of taking zero readings of the manometer, the impact-pressure probe was retracted into the wall of the reactor tube and the flow of water was shut off. The manometer was usually zeroed at half hour or 45 minute intervals. After the manometer was first zeroed, the impact-pressure probe was positioned by means of the micrometer head of the probe traversing mechanism; and manometer readings were taken for all of the required positions. The air temperature around the manometer was measured to determine the density difference of the manometer fluids; this density difference was used to convert the manometer readings to values of impact pressure. In view of the difference in the location of the static hole and the impact-pressure probe belonging to the same test section, the measured impact pressure had to be corrected for the frictional pressure drop between the two.

Friction factor tests were conducted similarly to the isothermal velocity profile tests. The only differences were that the transmission lines connected to the manometer came from static pressure holes at two different test sections.

Temperature and Velocity Profiles for Flow with Heat Transfer.--Few complications were introduced into the procedure used in the isothermal

velocity profile tests for the tests with combined flow and heat transfer. In order to insure steady state conditions hot water was circulated through the reactor jackets for at least an hour before the profile determinations were begun. To obtain zero readings of the manometer by stopping the flow would have disturbed the steady state, so the manometer reading taken at the center line of the reactor was used as a reference. The zero reading, h_{Mo}, was found by trial from the relations

$$2\int_0 s\hat{u}\ s\ ds = 1, \qquad u = \left[\frac{2\ g(\Delta\rho)_M\ (h_M - h_{Mo})}{\rho}\right]^{\frac{1}{2}} \tag{118}$$

where $(\Delta\rho)_M$ is the difference between the densities of the manometer fluids, h_M is the height gage reading, and g is the acceleration due to gravity.

Successive values of h_{Mo} were assumed, permitting points of $\hat{u}(s)$ to be plotted versus s. Smooth curves were drawn on the basis of these points, and the areas under the curves were integrated by means of Simpson's rule.

The temperature and impact-pressure measurements for a given test section were not obtained simultaneously. Ordinarily, the impact-pressure measurements were made first. When the temperature measurements were being made, a small flow rate, usually five to ten milliliters per minute, was set in the sampling line containing the thermocouple junction.

Temperature, Concentration and Velocity Profiles for Flow with Chemical Reaction.--A number of additional complications were introduced into the procedure when tests were made with chemical reaction. Two persons were

required to operate the equipment for these tests, and the presence of a third would have been helpful.

The first step in these tests was the preparation of sodium hydroxide solution. The 50 per cent sodium hydroxide was always diluted to 30 per cent or less, because the more concentrated solution has a substantial heat of dilution and would have caused a warmer reaction mixture in the mixing and profile development sections and thus a greater extent of the reaction at the first test section.

The second step was the preparation of sample receiving flasks for all the samples to be taken during the test. Each sample of the reaction mixture was taken in an Erlenmeyer flask containing a known amount of dilute hydrochloric acid and phenolphthalein indicator. The dilute acid stopped the reaction of methyl acetate for all practical purposes, since the rate coefficient for acid hydrolysis of methyl acetate is about 10 times the rate coefficient for saponification at the same temperature (151). The flask was weighed before and after sampling on a torsion balance which could be read ± 0.1 gram, and the weight of sample was determined by difference. The amount of sample taken was usually regulated to make the resulting mixture in the receiving flask very nearly neutral, but still acidic, in order to minimize the reaction of methyl acetate during the time that the flask stood before titration. The concentration of sodium hydroxide in the sample, as received in the flask, was determined by a back-titration with standard base.

After the sample flasks were prepared, the flow of water to the reactor was begun. As soon as the temperature of the water entering

the reactor came within 0.2°C of the temperature of the water issuing from the main, the flow of sodium hydroxide solution to the reactor was started. The flow rate of caustic was indicated by a calibrated rotameter and adjusted to give approximately the desired entrance concentration. The total flow rate of caustic solution and water was found by measuring the time required to collect a given weight of effluent. After ten minutes of caustic flow two samples were taken from the reactor via the sample probe and analyzed for sodium hydroxide content. Then the methyl acetate flow was begun, and the flow rate of effluent was redetermined. The caustic concentration in the entering reaction mixture could be calculated from these initial samples and flow rates with and without methyl acetate. The sampling flow rate was adjusted so that the volumetric flow rate was less than 80 per cent of the volumetric flow rate of that portion of the stream intercepted by the cross-sectional area of the probe tip.

After the methyl acetate had been flowing for about ten minutes, the sampling flow rate was measured and samples were taken at several positions of the sample probe. Potentiometer readings were made while the samples were being taken from the reactor. In addition, some readings were made after the samples were taken, usually with a lower flow rate in the sample probe.

The sample flasks were weighed and titrated as rapidly as possible after the samples were removed from the reactor. The time required to finish the analysis of a sample after it was taken was never more than about 20 minutes and usually around 10 minutes. Due to the dilution of the samples and the slight acidity of the contents of the sample flasks,

the errors caused by the time that the flasks were allowed to stand were less than 0.5 per cent of the true value.

In order to reduce the consumption of reactants, the flows of the reactants were shut off while samples were being analyzed. Then the reactant flows were re-started through the same procedure used initially.

Since the reaction proceeded as the sample traversed the length of the sampling line, the measured concentration of sodium hydroxide wass less than the concentration of the sample as it was drawn into the probe tip. This change in concentration was sufficiently large for it to be worth while to make a correction to the measured concentrations and thus estimate the true concentrations of the samples in the reactor. An approximate correction was made by using an average residence time and an average rate coefficient in the rate equations as integrated for a batch or plug-flow reactor:

$$\frac{C}{C_s} = \frac{1}{1 - C_s k_R t_s} \qquad (119a)$$

$$\frac{C}{C_s} \doteq \frac{1 + \delta_s k_R t_s}{1 - C_s k_R t_s}, \qquad \delta_s k_R t_s << 1 \qquad (119b)$$

Equation 119a is for equimolar reactants. In equation 119b C is the concentration of the limiting reactant, while δ_s is the difference between the concentrations of the two reactants. Such a correction is inexact, but it is clear from the publications of Cleland and Wilhelm (98) and of Horn and Kuechler (80) that the error in such

corrections would be an order of magnitude smaller than the corrections themselves.

The measurement of t_s, the apparent residence time in the sample line, and the choice of a temperature for the evaluation os k_R in equations 119 remain to be explained. A somewhat arbitrary procedure was used. The value of k_R was taken as that corresponding to the temperature measured by the thermocouple junction in the probe tip. The apparent residence time, t_s, was obtained from

$$t_s = \frac{V_s}{v_s}$$

where v_s is the volumetric flow rate in the sampling line and V_s is the apparent volume of the sampling line, which is assumed to be a constant for a given flow rate and temperature of coolant circulating through the sample cooler. Two or more samples were withdrawn for the same position, but with different sampling flow rates. Then V_s and C, the true sample concentration in the reactor were calculated from

$$\frac{1}{C_s} = \frac{1}{C} + k_R \frac{V_s}{v_s} \qquad (121)$$

A special test, number 6A, confirmed experimentally the linear relationship between $1/C_s$ and $1/v_s$ as shown in this equation. The apparent volume of the sample line was 0.78 milliliter without cooling. An <u>a priori</u> calculation, which neglected the drops and undispersed sample in the receiving flask, gave a volume of 0.53 milliliter. In the tests

with the more concentrated reaction mixture, the apparent residence time in the sampling line was about 0.3 second.

Interpretation of Experimental Data Near the Reactor Tube Wall.-- The measured impact pressures, temperatures, and concentrations are not really the time-average local values of these quantities that are desired, but represent some sort of averages over the volume of flow intercepted by the cross-sectional area of the respective probe tips. For this reason, in the presence of gradients of the measured quantities, an experimental value of one of the quantities may not be taken to be merely a true, time-averaged, local value at the center line of the probe. One would like to know the displacement from the tube wall where the time-averaged local value equals the value found by experiment. Such a displacement will be called a virtual displacement of a probe.

Young and Maas (152) measured the difference, δ_v, between the virtual displacement, y_v, of an impact-pressure probe and the displacement, y_o, of its center line in a transverse, impact-pressure gradient. They found that ". . . for a range of $(S/P_i)(dP_i/d\eta)$ from about 0.1 to 1.2, the ratio of δ_v/S is sensibly constant and independent of S_e, P_i, and $dP_i/d\eta$." Here, S and S_e are internal and external probe diameters, respectively, P_i is impact pressure, and η is displacement transverse to the direction of flow. Young and Maas found the ratio of δ_v/S to be given by

$$\delta_v/S = 0.131 + 0.082\, S_e/S \qquad (122)$$

under the conditions of their experiments. Equation 122 gives $\delta_v = 0.007$ inch for this investigation.

More recent measurements of δ_v were made by Macmillan (19, 153). He considers the effect of the viscosity of the fluid and the effects due to the presence of a solid boundary. Unfortunately, his corrections must be extrapolated beyond the range of his experiments to be applied to the small values of displacement in this thesis. However, the combination of his corrections for both effects, extrapolated where necessary, appears to give about the same values of δ_v as that obtained from equation 122.

Deissler (154) determined the position of a Pitot tube relative to a pipe wall by extrapolating experimental velocity curves to zero. This is equivalent to a determination of δ_v if the true displacement of the tube center line from the pipe wall is known. Values of δ_v determined by this method were within a range of 0.006 to 0.009 inch.

The displacement corrections were assumed to decrease for impact-pressure gradients below the range of the data of Young and Maas. This assumption may not be correct, but the resulting error relative to the displacement, y_o, is small in any event. The virtual displacement for the impact-pressure probes used in this investigation is given by

$$y_v = y_o + \delta_v, \qquad (S/P_i)(dP_i/dy) \geq 0.1$$

and (123)

$$y_v = y_o + \delta_v r/r_c, \qquad 0.1 > (S/P_i)(dP_i/dy) \geq 0$$

where r_c is the location of the probe center line when $(S/P_i)(dP_i/dy) = 0.1$.

The displacement corrections described above were for impact-pressure probes only. In addition, some simple estimates of the correction for the displacement of a sampling probe were made. The experimental temperatures and concentrations were assumed to be given by

$$T_e = \frac{\int_{y_o-r_p}^{y_o+r_p} uTz\, dy}{\int_{y_o-r_p}^{y_o+r_p} uz\, dy}, \qquad C_e = \frac{\int_{y_o-r_p}^{y_o+r_p} uCz\, dy}{\int_{y_o-r_p}^{y_o+r_p} uz\, dy} \tag{124}$$

Suppose that the curvature of the wall is negligible and assume that

$$u = \alpha_1 y, \quad T = T_1 - \alpha_2 y, \quad C = C_1 + \alpha_3 y \quad \text{for} \quad y \geq 0$$

and

$$u = 0 \quad \text{for} \quad y < 0$$

where α_1, α_2, α_3, T_1, and C_1 are constants.

Then, for $y_o = 0$

$$T_e = T_1 - \frac{3\pi\alpha_2 r_p}{16}, \tag{125a}$$

$$c = c_1 + \frac{3\pi\alpha_3 r_p}{16}, \tag{125b}$$

and

$$y_v = \frac{3\pi r_p}{16}; \tag{125c}$$

for $0 \leq y_o \leq r_p$

$$y = \frac{[(2/3)y_o(r_p^2 - y_o^2)^{3/2} + (\frac{1}{2})r_p^2 y_o^2 \cos^{-1}(-y_o/r_p) + (\frac{1}{2})y_o^3 (r_p^2 - y_o^2)^{\frac{1}{2}}}{(1/3)(r_p^2 - y_o^2)^{3/2} + (\frac{1}{2})y_o r_p^2 \cos^{-1}(-y_o/r_p) + (\frac{1}{2})y_o^2(r_p^2 - y_o^2)}$$
$$+ \frac{(1/8)r_p^4 \cos^{-1}(-y_o/r_p) + (1/8)y_o (r_p^2 - y_o^2)^{\frac{1}{2}} (2y_o^2 - r_p^2)]}{(1/3)(r_p^2 - y_o^2)^{3/2} + (\frac{1}{2})y_o r_p^2 \cos^{-1}(-y_o/r_p) + (\frac{1}{2})y_o^2(r_p^2 - y_o^2)}; \tag{126}$$

and for $y_o \geq r_p$

$$y_v = \frac{y_o^2 + r_p^2/4}{y_o} = y_o + r_p^2/4y_o . \qquad (127)$$

For the probes that were used, $r_p = 0.040$ inch and $y_v = 0.024$ inch or $y_v/r_w = 0.049$ at $y_o = 0$.

Estimation of Wall Temperatures.--The wall temperatures at the test sections were estimated for the tests made with heat transfer. First, the heat transfer coefficients were calculated for the fluid inside the reactor and for the fluid in the jackets by a formula obtained from McAdams (155),

$$\frac{h_{TL}}{Z_b G_m} = 0.023(N_{Pr})_b^{-2/3} (N_{Re})_b^{-0.2} (\mu_b/\mu_w)^{0.14} \qquad (128)$$

where h_{TL} is the heat transfer coefficient, G_m is the mass flow rate, and the subscripts b and w refer to properties evaluated at the bulk and wall temperatures, respectively. A value of 9.4 BTU/(hr.) (sq. ft.) (deg. F) was used for the conductivity of stainless steel (156). From this and the transfer coefficient, relative resistances of the reactor wall and of the fluid on either side were calculated. Then, assuming that the ratio of one relative resistance to the sum of the relative resistances equals the ratio of the corresponding temperature difference to the total difference in the bulk temperatures of the fluids, the temperature of the reaction mixture at the wall was estimated.

Experimental Conditions.--A summary of the conditions in all of the tests made for the experimental part of this investigation is shown in Table 5. Note that computer simulations were not carried out for every test shown. Calculations corresponding to the heat transfer test identified by HT2 were omitted because this was almost a duplication of HT1. Instead, two of Sleicher's experimental heat transfer runs were simulated. The calculations for reaction tests R3H, R4A, and R4H were omitted because the low concentrations in these cases made them considerably less interesting than the tests at greater concentrations.

Experimental Determination of Physical Data.--The effects of changes in temperature and extent of reaction on some of the physical properties of the experimental reaction mixtures were determined. Solutions were prepared corresponding to the initial and final compositions of equimolar reaction mixtures having approximate molarities of 1.0, 2.0, and 3.0. Since the compositions of actual reaction mixtures could not be held constant, the solutions corresponding to the initial compositions of these reaction mixtures were made by substituting an equal number of moles of methanol for methyl acetate. Since the methyl acetate was assumed to be in a 50 weight per cent methanol solution, the simulated initial reaction mixtures had molarities with respect to methanol which were about 3.3 times those with respect to sodium hydroxide. The actual compositions of imitation reaction mixtures are given in Table 6.

Table 5. Experimental Conditions

Identifier of Test	Feed Temp., °C	$\bar{u}$, cm./sec.	N_{Re} at Inlet	Jacket Temp., °C (Average)	Inlet Temp., °C[1] (Average)	Concentrations, Moles/Liter			
						Feed		Reactor Inlet[1] (Average)	
						NaOH	$C_3H_6O_2$	$NaOH_2$	$C_3H_6O_2$
V1		20.7	4,800	-					
V2		20.75	5,040	-					
V3		20.65	4,880	-					
V5		43.0	10,150	-					
V6		43.0	10,420	-					
V7		47.2	10,510	-					
HT1	15.2	26.1	5,560	40.5	15.2				
HT2	14.0	25.1	5,210	50.5	14.0				
HT3	9.0	51.7	9,500	50.5	9.0				
R3HT	15.1	23.3	4,470	51.5	15.9	0.184	0.201	0.164	0.181
R4A	14.5	46.6	8,740	[2]	14.5	0.192	0.204	0.176	0.188
R4H	14.5	46.6	8,740	50.5	14.5	0.192	0.204	0.176	0.188
R5A	10.0	35.4	4,620	[2]	10.1	0.479	0.531	0.419	0.471
R5H	9.6	35.4	4,620	50.5	9.7	0.479	0.531	0.419	0.471
R6A	14.9	55.0	8,600	[2]	15.0	0.539	0.507	0.459	0.427
R6H	14.9	55.0	8,600	51.0	15.0	0.539	0.507	0.459	0.427
R7A	22.1	36.2	4,890	[2]	25.6	1.151	1.030	0.659	0.538
R7H	19.9	36.1	5,410	51.0	23.6	1.080	1.003	0.672[3]	0.595[3]
R8	15.5	31.3	5,110	[2]	15.5	0.478	0.493	0.379	0.394

[1]These values were measured at the first test section, which is considered the reactor inlet.

[2]Water was not circulated through the reactor jackets during these runs. The water in the jackets was at the temperature of the surrounding air.

[3]Calculated by means of the equation for piston-flow reactor using an average temperature.

Table 6. Compositions of Imitation Reaction Mixtures

Identifier of Mixture	Concentrations, Moles per Liter		
	NaOH	CH_3COONa	CH_3OH
1A	0.95	----	3.31
2A	1.92	----	6.61
3A	2.97	----	9.99
1B	----	1.00	3.31
2B	----	2.00	6.62
3B	----	2.99	9.94

Viscosities of all solutions were determined at 5.1°C, 30.5°C and 51.95°C. Two Cannon-Ostwald-Fenske viscosimeters previously calibrated with water were used for these determinations. Specific gravities of the solutions were measured with hydrometers at the same temperatures as the viscosities. Measurements of values of the thermal conductivity of solutions 1B and 3B were supplied by Mr. J. A. McAlister (157) of the Micromeritics Branch, Georgia Tech Engineering Experiment Station.

CHAPTER V

RESULTS

The first part of this chapter deals with the results of experiments, the input data and results of theoretical calculations made for the simulation of these experiments, and the sources of data used in these calculations. The second part is devoted to deductions concerning approximate chemical similarity that may be made from the mathematical model used in this thesis and other models. Finally, the results of illustrative calculations concerning parametric sensitivity and thermal initiation are presented.

Experimental and Theoretical Results

The experimental data obtained in the investigation described in Chapter IV are presented in this section. Wherever comparable results were obtained by calculations using the mathematical model of this thesis, both the experimental data and the results of calculation are presented in the same figure or the same table. The results of the experimental tests are considered in the following order: flow without heat transfer or chemical reaction flow;with heat transfer, but without chemical reaction; flow with chemical reaction and little or no heat transfer; and flow with both chemical reaction and heat transfer.

Data and Results of Calculation.--The experimental data for isothermal flow have been summarized in two tables and two figures. Experimental

values of the Fanning friction factor are presented in Table 7. Experimental values of $\bar{u}/u_{max}$ are reported in Table 8. These may be compared with the correlations of experimental data that are given in Table 3. The experimentally-determined, temporal-mean velocity distributions for Reynolds numbers of 5,000 and 10,000 are presented in Figures 5 and 6, respectively. These data are also tabulated for reference in Appendix III.

Velocity distributions calculated from equation 106b for Reynolds numbers of 5,000 and 10,000 are also presented in Figures 5 and 6. Additional computed velocity distributions for Reynolds numbers of 19,500 and 39,500 are shown in Figures 7 and 8 along with comparable experimental data. The corresponding distributions of eddy diffusivity of momentum and Prandtl's mixing length parameter calculated from equations 98, 101, and 103 may be found in Figures 9 and 10, respectively.

Experimental tests concerning flow with heat transfer yielded temperature- and velocity-distribution data. The temperature distributions obtained in heat transfer tests HT3 and HT1 are presented in Figures 11a and 11b, respectively. In addition, the experimental data from Sleicher's (13) runs HTS10 and HTS5 are shown in Figures 11c and 11d, respectively. Experimental velocity-distribution data for flow with and without heat transfer at a Reynolds number of about 10,000 are presented in Figure 12. Data of this type were also obtained for flow at a Reynolds number of 5,000; but since none of these data are sufficiently precise to determine quantitatively the change in velocity distribution, the data for the lower Reynolds number have been omitted.

Table 7. Experimental Friction Factor Data

N_{Re}	f_F
1,640	0.0107
3,800	0.0104
5,900	0.00927
8,100	0.00864
10,340	0.00829
12,470	0.00772

Table 8. Experimental Values of $\bar{u}/u_{max}$

N_{Re}	$\bar{u}/u_{max}$
4,800	0.753
4,880	0.764
10,150	0.788
10,420	0.780
10,510	0.782

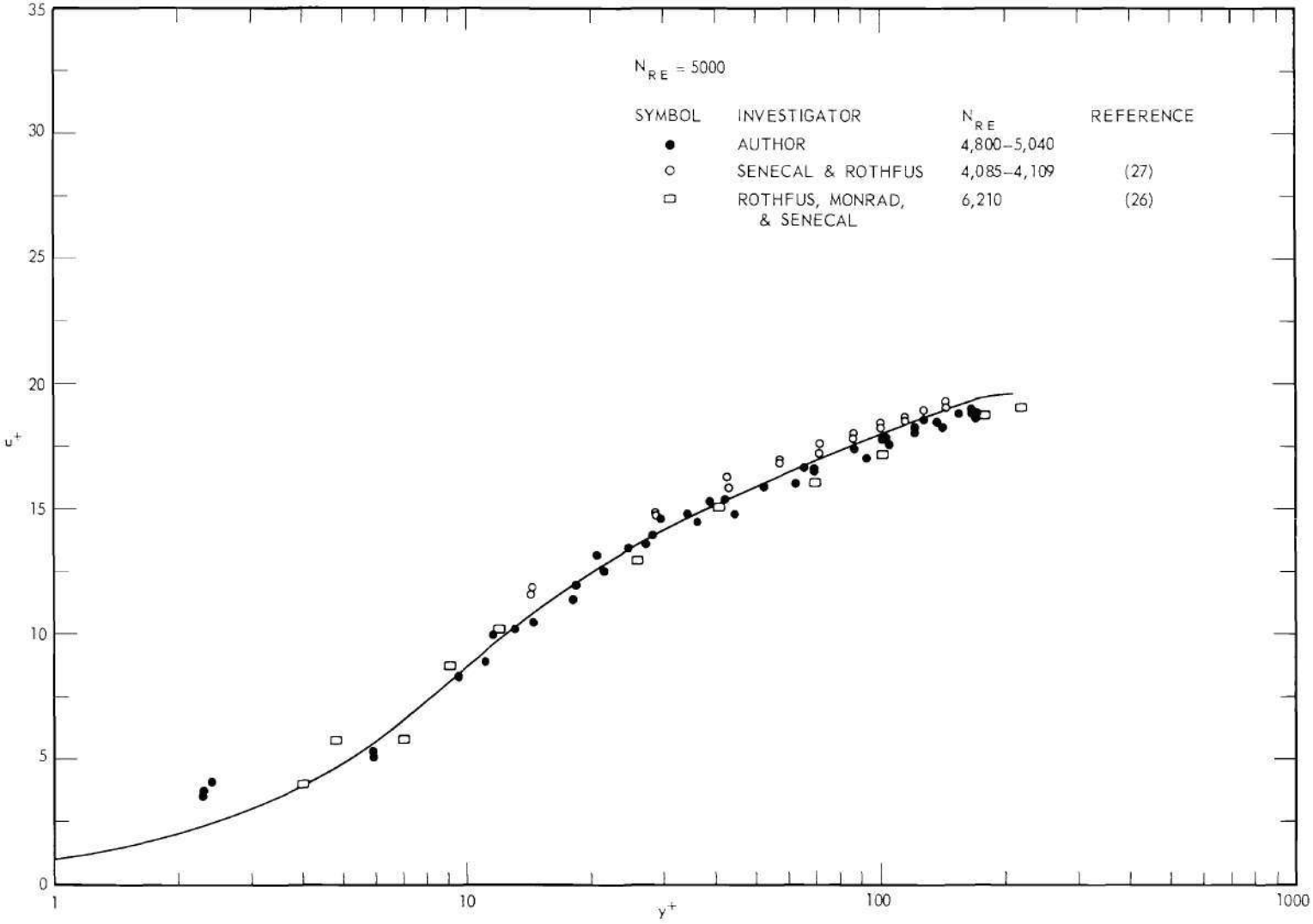

Figure 5. Velocity Distribution for N_{RE} = 5000.

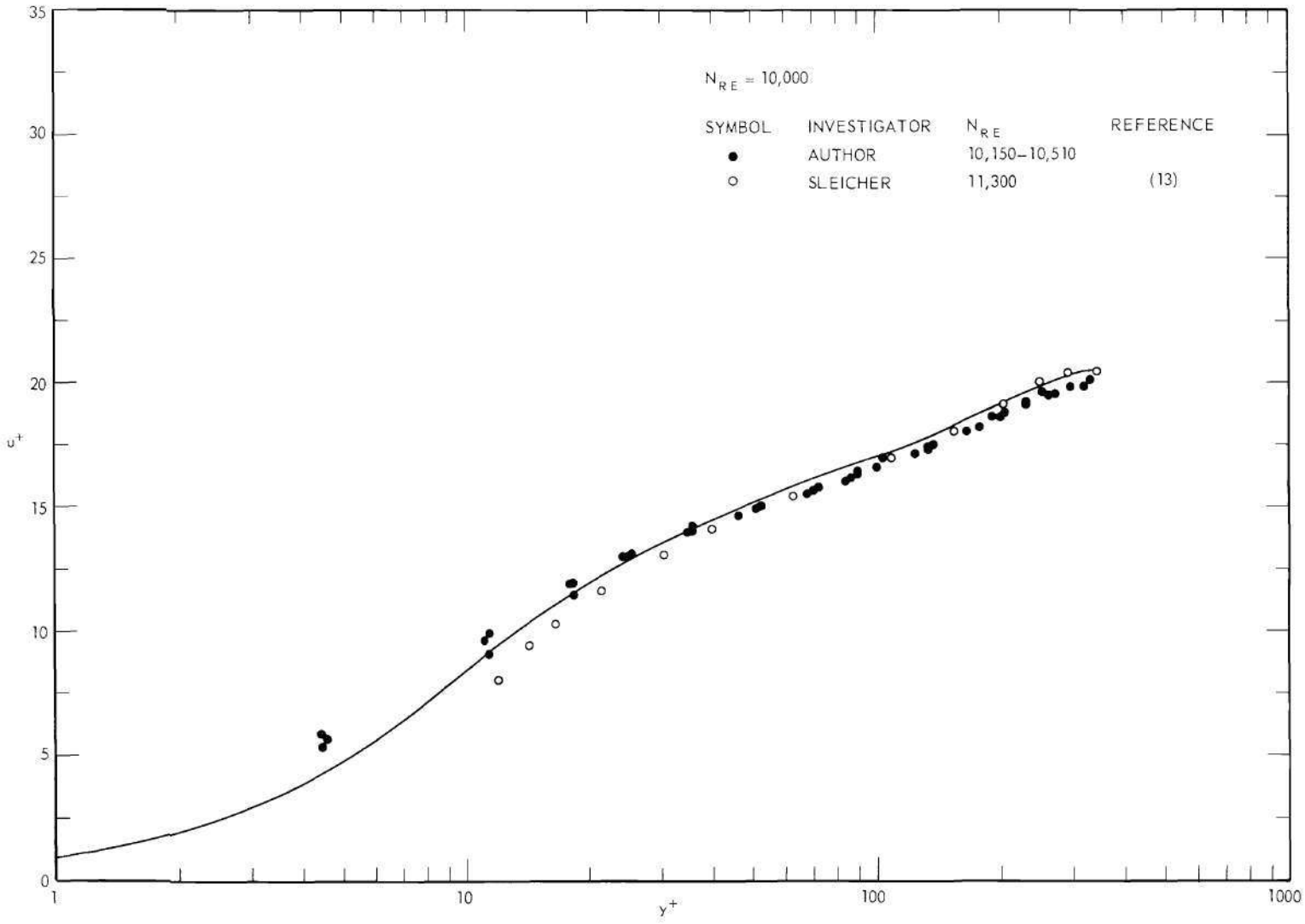

Figure 6. Velocity Distribution for N_{RE} = 10,000.

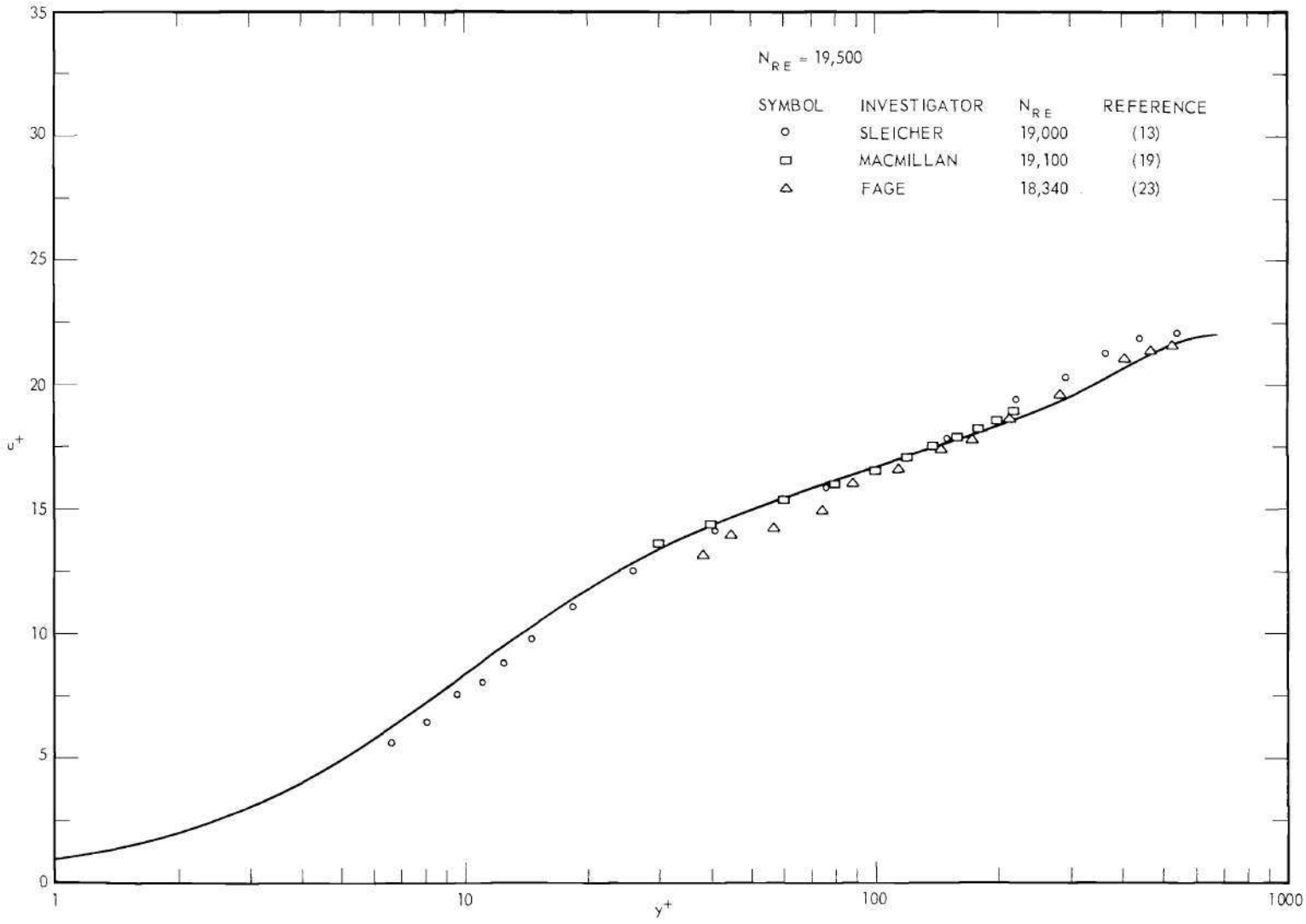

Figure 7. Velocity Distribution for N_{RE} = 19,500.

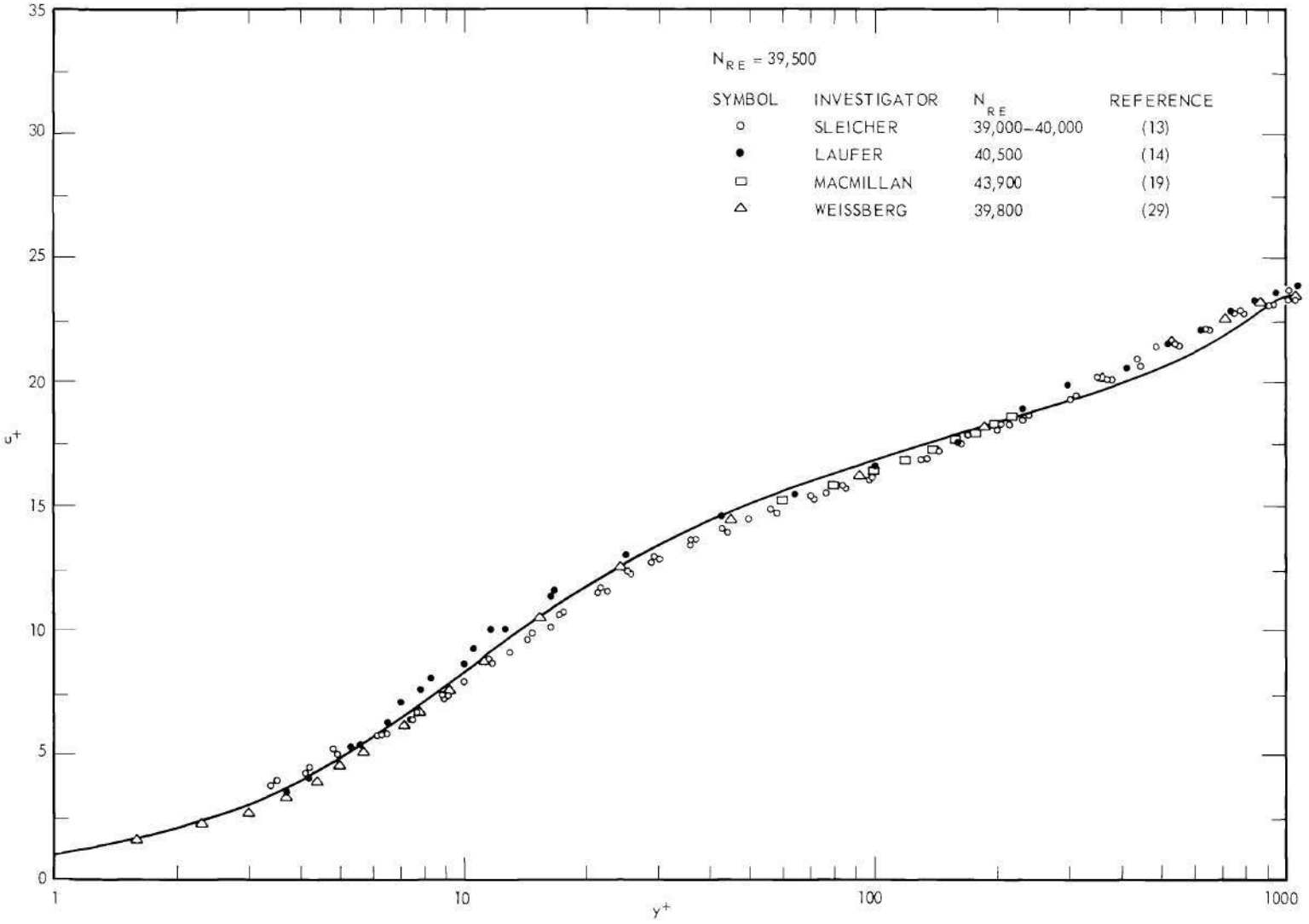

Figure 8. Velocity Distribution for N_{RE} = 39,500.

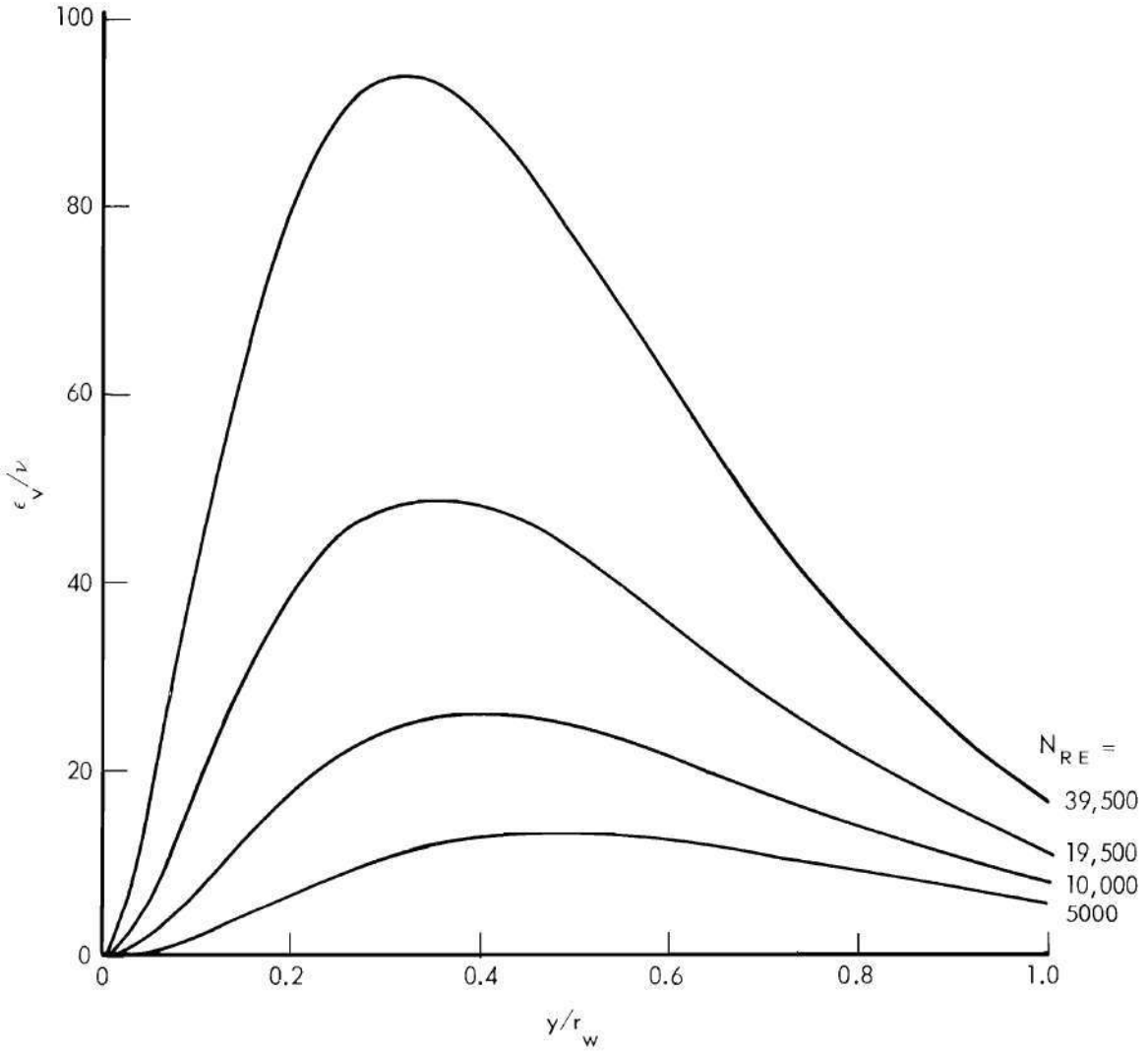

Figure 9. Eddy Diffusivity Distributions.

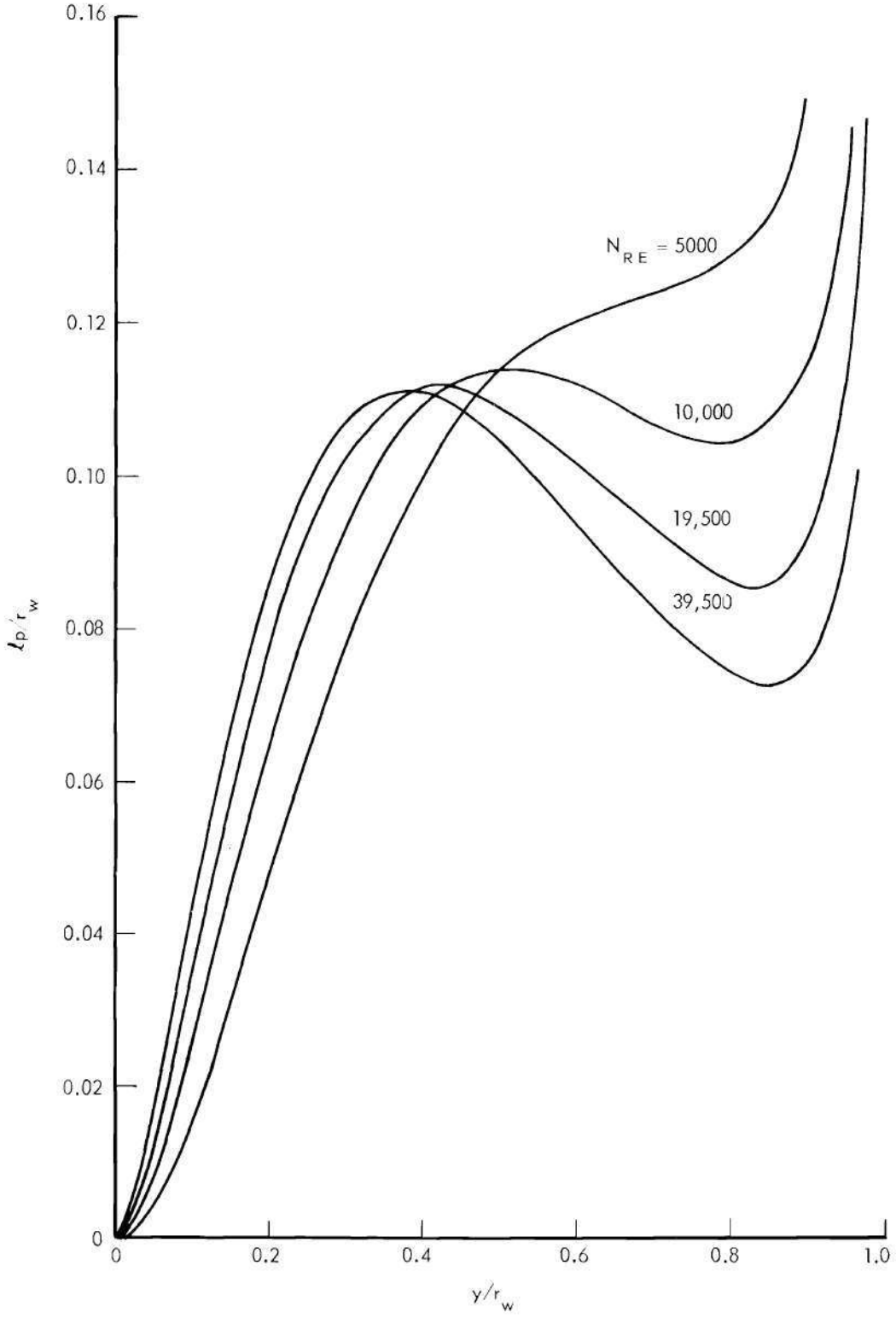

Figure 10. Mixing Length Distributions.

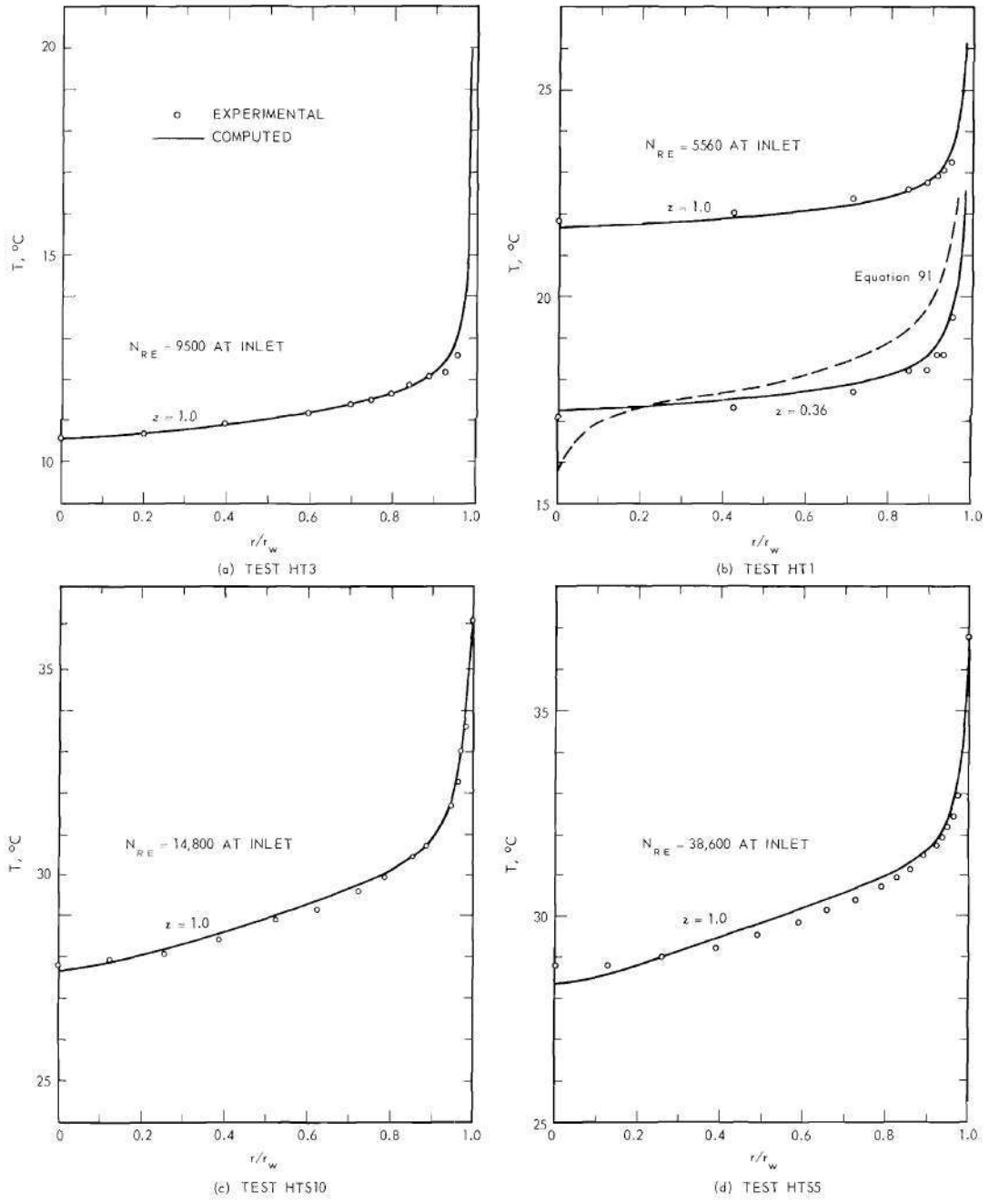

Figure 11. Experimental and Computed Temperature Distributions.

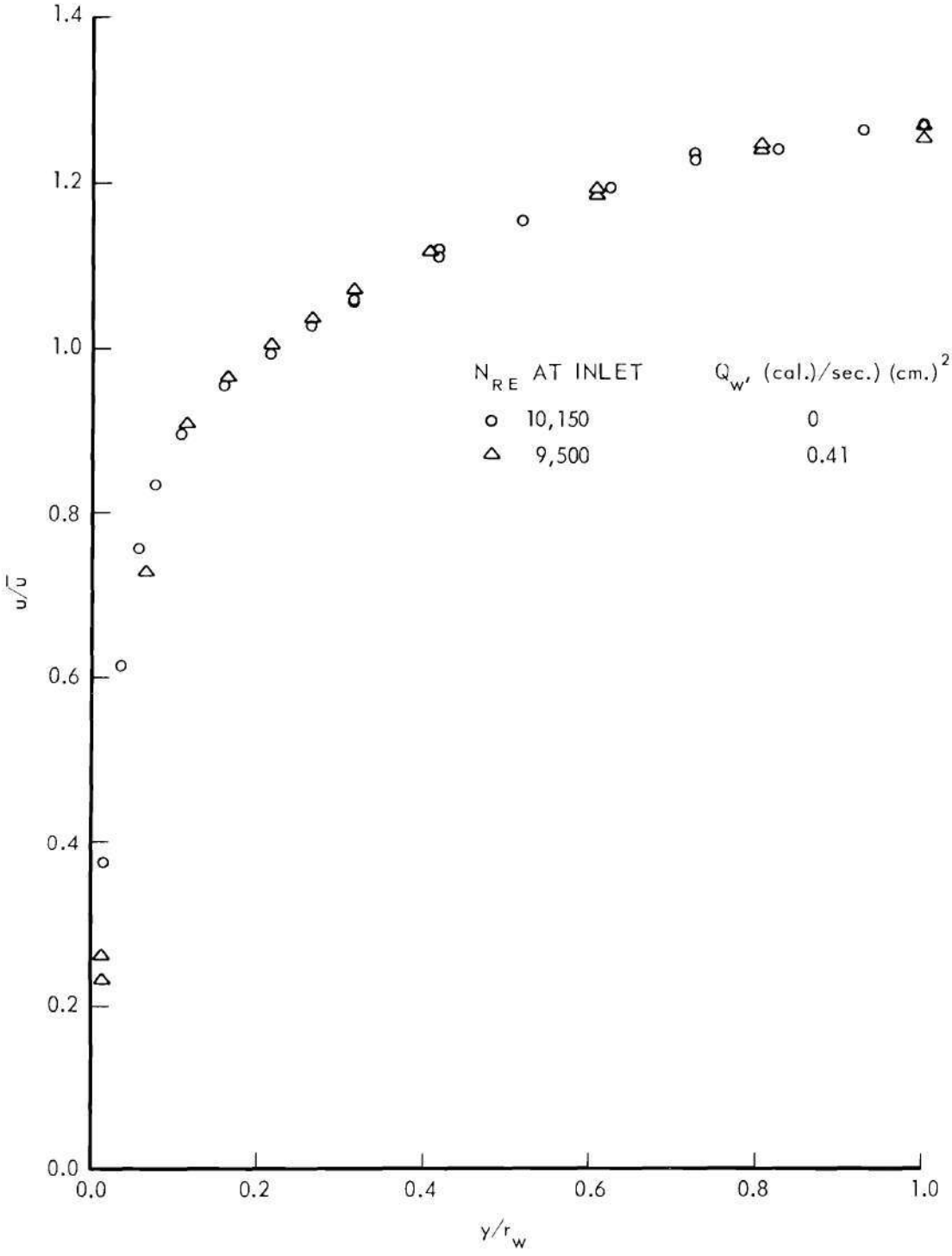

Figure 12. Velocity Distributions for Flow with and without Heat Transfer.

Velocity data obtained for flow with chemical reaction have been omitted for the same reason.

Computed temperature distributions obtained in simulations of HT1, HT3, HTS5, and HTS10 are presented in the same figures as the corresponding experimental data. The input data for these calculations may be found in Table 9. The values of thermal conductivity appearing in the tabulated values of parameter A_x and the thermal diffusivity correspond to the arithmetic average of the wall temperature at the inlet and outlet of the reactor. The values of viscosity and density in this table correspond to the arithmetic average of the bulk temperatures at the inlet and outlet of the reactor. The data for the simulation of HTS5 and HTS10 were taken from Sleicher's thesis and Tribus and Boelter (158).

The results obtained from pseudo-adiabatic chemical-reaction tests R4A, R5A, R6A, R7A, and R8 consist of concentration and temperature distributions. As expected, the measurements of these tests showed that the radial variations of temperature and concentration were negligible throughout most of the cross sectional area of the reactor tube. For this reason, the full profiles are not presented, but the averages of the experimental values for the profiles are presented in Table 10.

The computed concentrations and temperatures corresponding to the pseudo-adiabatic chemical-reaction tests are also given in Table 10. As before, the input data for these calculations may be found in Table 9. Table 10 also includes the concentrations calculated by means of the equation for a piston-flow reactor. In these calculations the rate coefficient was evaluated at the arithmetic average of the bulk temperatures of the initial and final cross sections.

Table 9. Input Data for Calculations. Part 1.

	Units	Identifier						
		HT1	HT3	HTS5	HTS10	R5A	R5H	R6A
c_1^o	mole/liter	1.0	1.0	1.0	1.0	0.419	0.419	0.437
Δ_s	-	0	0	0	0	0.124	0.124	0.073
T^o	°C	15.1	9.1	26.5	25.7	10.2	9.3	15.15
T_J(initial)	°C	40.7	51.1	36.8	37.2	20.0	51.3	20.0
r_w	cm.	1.22	1.22	1.91	1.91	1.22	1.22	1.22
L	cm.	336	122	118.4	118.4	346	346	346
$\bar{u}$	cm./sec.	26.1	51.7	1605	587	35.4	35.4	55.0
$\nu \times 10^{-2}$	$(cm.)^2/sec.$	1.03	1.28	15.9	16.0	1.72	1.56	1.48
ρ^*	$gm./(cm.)^3$	1.0	1.0	1.17×10^{-3}	1.16×10^{-3}	1.01	1.01	1.01
Z*	(cal.)/(gm.)(°C)	1.0	1.0	0.2402	0.2403	1.0	1.0	1.0
$K_m \times 10^{-3}$	$(cm.)^2/sec.$	1.465	1.45	232.0	231.0	1.31	1.42	1.34
$D_m \times 10^{-3}$	$(cm.)^2/sec.$	0.01	0.01	200.0	200.0	0.01	0.01	0.01
E/R_g	$(°K)^{-1}$	100	100	100	100	5918	5918	5918
B	-	0	0	0	0	18.095	18.095	18.095
$H_R/Z\rho$	(°C)(liter)/equivalent	0	0	0	0	-14.05	-14.05	-14.05
A_x	$(cal.)/(cm.)^2(sec.)(°C)$	24.0	22.0	1.0×10^5	1×10^{-5}	1.0	24.5	1.0
α_H	-	1.4	1.3	1.15	1.25	1.43	1.41	1.32
α_M	-	1.4	1.3	1.15	1.25	1.43	1.41	1.32
Order	-	-				2	2	2

* Values of ρ and Z were not required as input data, but have been shown wherever available.

Table 9. Input Data for Calculations. Part 1 (Continued)

	Units	Identifier						
		R6H	R7A	R7H	R8	BA1	BA2	BA3
c_1^o	mole/liter	0.437	0.538	0.595	0.379	20	20	20
Δ_s	-	0.073	0.225	0.146	0.040	0	0	0
T^o	°C	15.15	25.6	23.6	17.8	67	67	67
T_J(initial)	°C	51.5	20.0	51.4	20.0	25	25	25
r_w	cm.	1.22	1.22	1.22	1.22	1.0	1.0	1.0
L	cm.	346	346	346	346	2000	500	500
$\bar{u}$	cm./sec.	55.0	36.2	36.1	31.35	100	100	200
$\nu \times 10^{-2}$	$(cm.)^2/sec.$	1.36	1.47	1.42	1.43	2.0	2.0	2.0
ρ^*	$gm./(cm.)^3$	1.01	1.02	1.02	1.01	-		
Z^*	(cal.)/(gm.)(°C)	1.0	1.0	1.0	1.0	-		
$K_m \times 10^{-3}$	$(cm.)^2/sec.$	1.43	1.33	1.38	1.36	1.0	1.0	1.0
$D_m \times 10^{-3}$	$(cm.)^2/sec.$	0.01	0.01	0.01	0.01	0.01	0.01	0.01
E/R_g	$(°K)^{-1}$	5918	5918	5918	5918	11,324	11,324	11,324
B	-	18.095	18.095	18.095	18.095	30.345	30.345	30.345
$H_R/Z\rho$	(°C)(liter)/equivalent	-14.05	-14.05	-14.05	-14.05	-10.0	-10.0	-10.0
A_x	(cal.)/$(cm.)^2$(sec.)(°C)	24.5	1.0	27.5	1.0	1400	1400	1400
α_H	-	1.30	1.42	1.42	1.42	1.3	1.3	1.3
α_m	-	1.30	1.42	1.42	1.42	1.3	1.3	1.3
Order	-	2	2	2	2	1	1	1

*Values of ρ and Z were not required as input data, but have been shown wherever available.

Table 9. Input Data for Calculations. Part 1 (Continued)

	Units	Identifier							
		BA4	BA5	BA6	BA7	BA8	TIN1	TIN2	TIX
c_1^o	mole/liter	20	20	20	20	20	4.0	4.0	4.0
Δ_s	-	0	0	0	0	0	0	0	0
T^o	°C	67	67	67	67	67	30	30	30
T_J(initial)	°C	35	15	45	55	60	30	30	30
r_w	cm.	1.0	1.0	1.0	1.0	1.0	4.0	4.0	4.0
L	cm.	500	500	500	500	500	2000	4000	4000
$\bar{u}$	cm./sec.	200	200	200	200	200	100	200	200
$\nu \times 10^{-2}$	$(cm.)^2/sec.$	2.0	2.0	2.0	2.0	2.0	10.0	10.0	10.0
ρ^*	$gm./(cm.)^3$						-		
Z*	(cal.)/(gm.)(°C)						-		
$K_m \times 10^{-3}$	$(cm.)^2/sec.$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$D_m \times 10^{-3}$	$(cm.)^2/sec.$	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
E/R_g	$(°K)^{-1}$	11,324	11,324	11,324	11,324	11,324	8000	8000	8000
B	-	30.345	30.345	30.345	30.345	30.345	18.0	18.0	18.0
$H_R/Z\rho$	(°C)(liter)/equivalent	-10.0	-10.0	-10.0	-10.0	-10.0	15.0	15.0	-15.0
A_x	$(cal.)/(cm.)^2(sec.)(°C)$	1400	1400	1400	1400	1400	160.0	160.0	160.0
α_H	-	1.3	1.3	1.3	1.3	1.3	1.35	1.28	1.28
α_m	-	1.3	1.3	1.3	1.3	1.3	1.35	1.28	1.28
Order	-	1	1	1	1	1	2	2	2

*Values of ρ and Z were not required as input data, but have been shown wherever available.

Table 9. Input Data for Calculations. Part 2

	Identifiers				Identifier of Calculation			
	HT1		HT3		R5H		R6H	
Initial jacket temperature °C		40.7		51.1		51.3		51.5
Temperature control programs; units: T_J, °C; $z = x/L$, dimensionless	z	$\Delta T_J/\Delta z$	z	$\Delta T_J/\Delta z$	z	$\Delta T_J/\Delta z$	z	$\Delta T_J/\Delta z$
	0.0	- 3.6	0.0	- 2.3	0.0	- 4.45	0.0	- 4.85
	0.36	70.0			0.36	82.5	0.36	92.5
	0.38	0.0			0.38	0.0	0.38	0.0
	0.64	- 30.0			0.64	- 52.5	0.64	- 60.0
	0.66	- 0.9			0.66	- 2.85	0.66	- 3.5

Table 9. Input Data for Calculations. Part 2 (Continued)

	Identifier of Calculation							
	R7H		TIN1		TIN2		TIX	
Initial jacket temperature °C		51.4		30.0		30.0		30.0
Temperature control programs; units: T_J, °C; $z = x/L$, dimensionless	z	$\Delta T_J/\Delta z$	z	$\Delta T_J/\Delta z$	z	$\Delta T_J/\Delta s$	z	$\Delta T_J/\Delta z$
	0.0	- 2.5	0.0	0.0	0.0	0.0	0.0	0.0
	0.36	60.0	0.02	4000.0	0.02	4000.0	0.02	4000.0
	0.38	0.0	0.05	0.0	0.07	0.0	0.05	0.0
	0.64	- 30.0	0.90	- 4000.0	0.90	- 4000.0	0.20	- 1000.0
	0.66	- 1.15	0.93	0.0	0.95	0.0	0.28	0.0
							0.97	- 2000.0
							0.99	0.0

Table 10. Comparison of Conversions for Pseudo-Adiabatic Operation

Identifier	Inlet Values			Average k_R, $\frac{\text{liter}}{(\text{sec.})(\text{mole})}$	Final Concentrations, moles/liter		
	N_{Re}	Concentration of Limiting Reactant, Moles/liter	Δ_s		Radial-diffusion	Piston-flow	Experiment
R5A	4620	0.419	0.124	0.066	0.320	0.320	0.332
R6A	8600	0.437	0.073	0.094	0.320	0.341	0.330
R7A	4890	0.538	0.225	0.203	0.212	0.214	0.254
R8	5110	0.379	0.040	0.112	0.324	0.324	0.305

The experimental data for chemical reaction and heat transfer tests R5H, R6H, and R7H consist of concentration and temperature distributions. These are presented in Figures 13 and 14.

Computed concentration and temperature distributions corresponding to tests R5H, R6H, and R7H are also shown in Figures 13 and 14. The input data for these calculations may be found in Table 9. Values of thermal conductivity, viscosity, and density used for these calculations were averaged in the same way as for the calculations corresponding to the heat transfer tests.

Sources of Data Used in Calculations.--Experimental heat transfer and reaction trials are simulated to allow a comparison of computed and experimental results. All of the input data shown for these trials in Table 9 were obtained in the experimental part of this investigation except for the constants in the expression for the reaction rate coefficient, the heat of reaction, the ratios $\varepsilon_H/\varepsilon_v$ and $\varepsilon_m/\varepsilon_v$, and the quantities Z, D_m, and h_{Tx}. The experimental determination of viscosities, densities, and thermal conductivities of imitation reaction mixtures is described in Chapter IV. These results are presented in Figures 15, 16 and 17.

The kinetic data reported by Reicher (159) and Skrabal and Hugetz (160) are used. More recent data have been obtained by Rylander and Tarbell (161) and Newling and Hinshelwood (162), both using an aqueous acetone medium. These data confirm the activation energy obtained from Reicher and Skrabal and Hugetz, but the values for the rate coefficient are lower, presumably because of the solvent. Olsson (163) also reported a value of the rate coefficient, but it is not clear whether

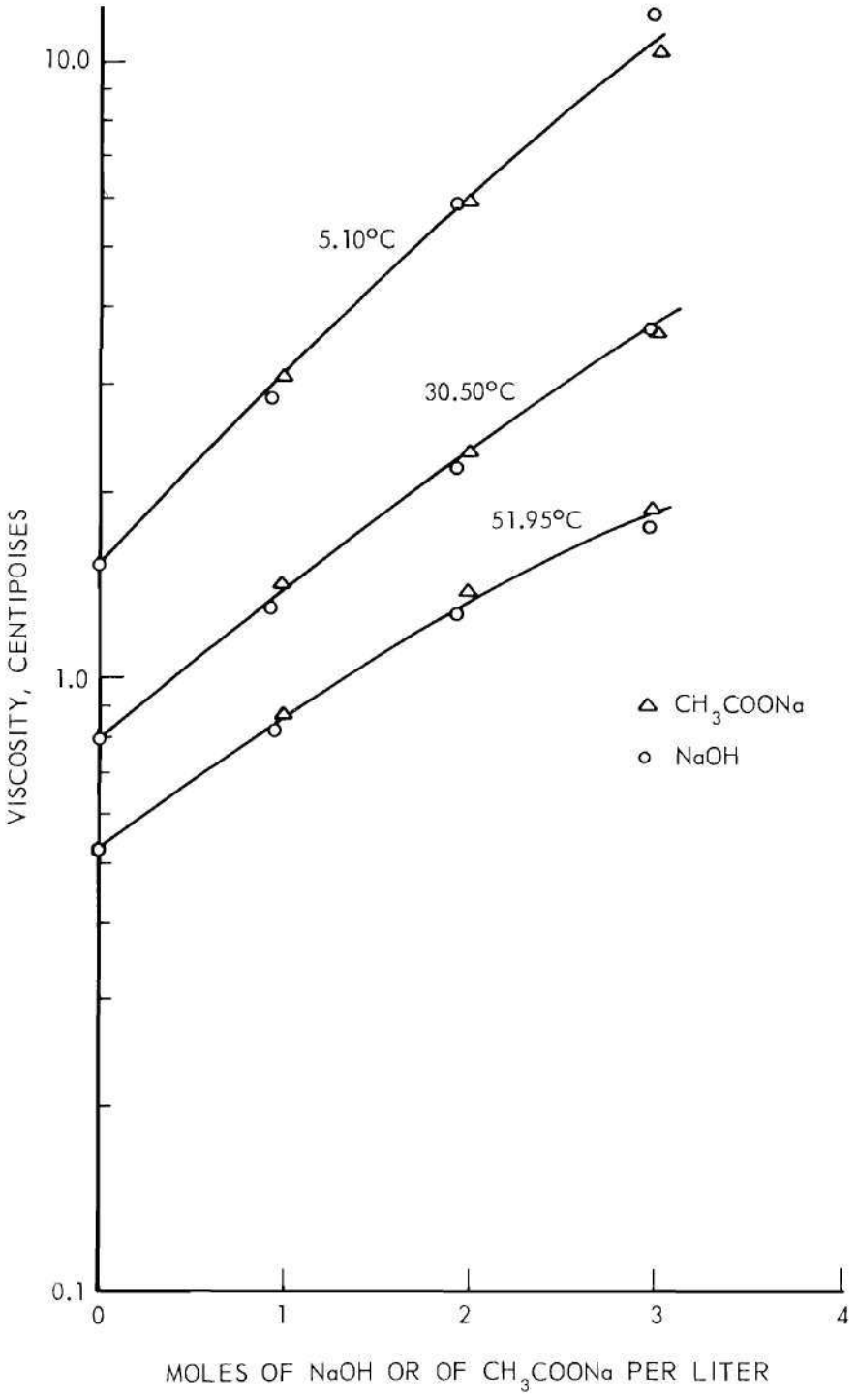

Figure 15. Viscosities of Imitation Reaction Mixtures.

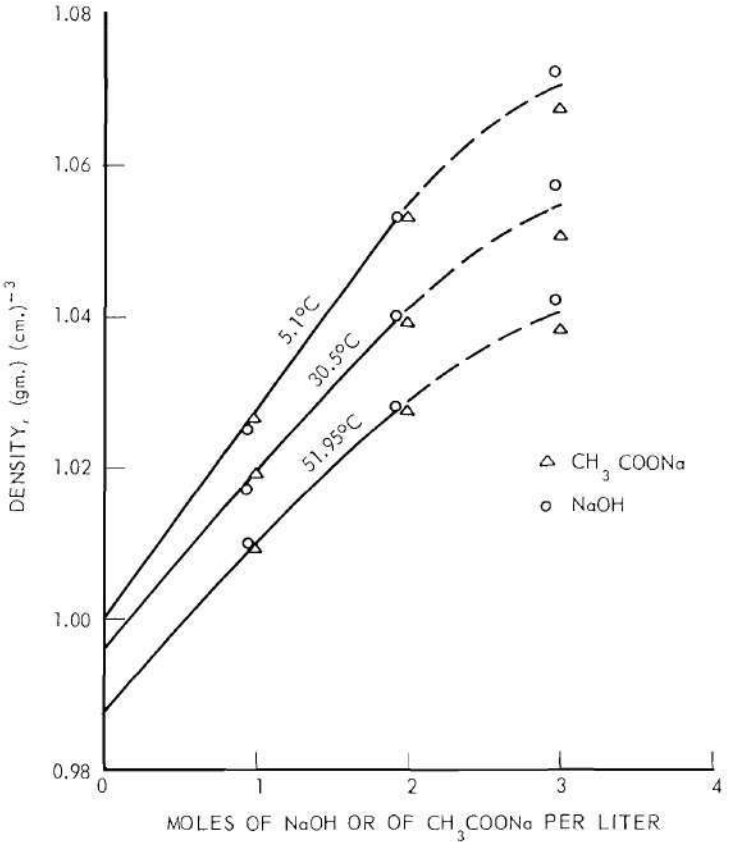

Figure 16. Densities of Imitation Reaction Mixtures.

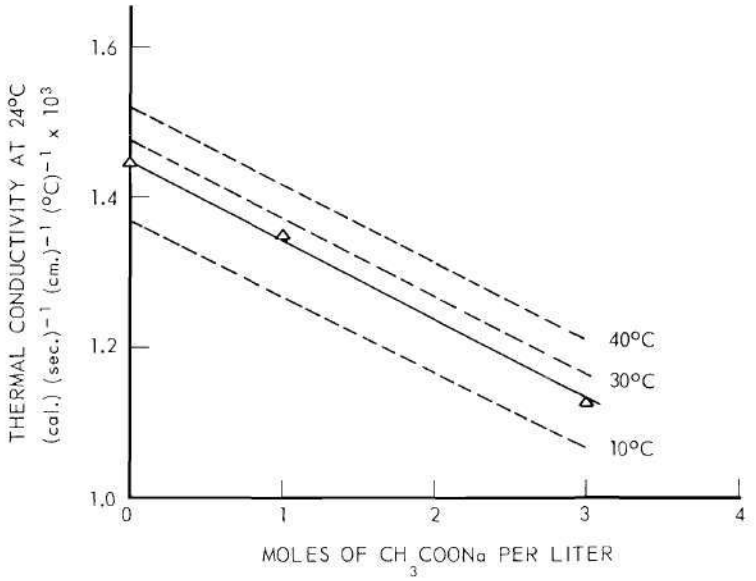

Figure 17. Thermal Conductivities of Imitation Reaction Mixtures.

this represented independent experimental data or whether it was calculated from the data reported by Skrabal and Hugetz and Reicher.

The heat of reaction was obtained from the aqueous heats of formation of OH^-, CH_3COO^-, CH_3OH, and $CH_3COO\,CH_3$. The values for the first three of these were obtained from Circular 500 of the National Bureau of Standards (164). The standard heat of formation of methyl acetate was estimated by the method of Franklin, described in Reid and Sherwood (165). The heat of formation of aqueous methyl acetate was obtained from this estimate and an estimate of the heat of solution made by the method of Moelwyn-Hughes (166) using the partial pressure data of Marshall (167). The estimated heat of solution appeared to be reasonable by comparison with the heats of solution of other methyl and ethyl esters reported in the International Critical Tables.

The values of $\varepsilon_H / \varepsilon_v$ and $\varepsilon_m / \varepsilon_v$ are obtained from equation 104. The heat capacities and the effect of temperature on the thermal conductivities of all reaction mixtures are assumed to be the same as those for water at the same temperatures. Since all of the reaction mixtures contained at least 85 weight per cent water and included both organic and inorganic constituents, the errors introduced by this assumption should be small. An average value of the molecular diffusivity was obtained from data given in Reid and Sherwood (167).

The external heat transfer coefficient, h_{Tx}, was first estimated roughly by equation 128 on the basis of experimental temperatures and flow data. The values of h_{Tx} required to give agreement between experimental temperatures and the temperatures obtained from simulated heat

transfer runs were determined by trial. The latter values were about 20 per cent less than the rough estimates obtained from equation 128. This difference can be attributed to errors in the experimental values of flow-rates, peculiarities in the geometry of the jackets, the inexactness of equation 128, and the error caused by the use of finite approximations to derivatives in the vicinity of the reactor wall.

Approximate Chemical Similarity

The equations of the radial-diffusion model of this thesis can be used to deduce conditions for approximate chemical similarity in prototype and model reactors. One can also use the equations of an axial-diffusion model for this, so that one obtains an interesting comparison between the two kinds of mathematical models.

The conditions of approximate chemical similarity for isothermal reactions can be obtained from equation 106b if the functions $\hat{u}(s)$ and $\hat{D}(s)$ are assumed to be independent of Reynolds number. Then equation 106b and its boundary conditions 107a, 107b, and 107c imply that chemical similarity for a reaction proceeding in two different reactors can be obtained by having the same values of P_2, Q_2, and the boundary conditions for both reactors. The use of these conditions for approximate chemical similarity in tubular reactors will be illustrated.

Consider an isothermal reaction proceeding in two reactors operating under conditions of chemical similarity. The production rates differ by a scale factor, X, that is

$$\frac{\pi_2}{\pi_1} = X = \frac{(Lr_w^2)_2}{(Lr_w^2)_1} \tag{129}$$

The invariance of Q_2 implies that $(L/\bar{u})_1 = (L/\bar{u})_2 = t_R$, since the inlet concentration and density are the same for both cases. From the invariance of P_2, equation 129 and the definition of the Reynolds number, one gets

$$(r_w)_2 = \left[\frac{D^* t_R}{P_1}\right]^{\frac{1}{2}} \tag{130a}$$

and

$$(r_w)_2 (N_{Re})_2 = \frac{(N_{Re})_1 \times (L r_w^2)_1}{t_R (r_w \bar{u})_1} \tag{130b}$$

These equations and the relationship between D^* and N_{Re} permit the size and flow rate for one reactor to be calculated from the other. For example, suppose that for the prototype one has the conditions:

$$r_w = 2.12 \text{ cm.}, \qquad \bar{u} = 118.0 \text{ cm./sec.}$$

$$N_{Re} = 25{,}000, \qquad L = 1180 \text{ cm.}$$

Then if D^* is related to N_{Re} by equations 98, 101, and 103 and $X = 0.1$, the conditions of chemical similarity in the model are shown in Table 11 under the heading Model 1. Of course, the changes in the distributed parameters $\hat{a}(s)$ and $\hat{D}(s)$ resulting from the change in the value of the Reynolds number prevent these conditions for chemical similarity from being more than an approximation.

Conditions for approximate chemical similarity can also be found for non-isothermal reactions in adiabatic reactors provided that K^* and D^* are very nearly equal. This is true for many liquids and

Table 11. Comparison of Models for Approximate Chemical Similarity

	Prototype	Model 1	Model 2	Model 3
r_w, cm.	2.12	1.01	0.92	0.685
$\bar{u}$, cm./sec.	118.0	51.5	62.7	113.0
N_{Re}	25,000	5200	5770	7750
L, cm.	1180.0	515.0	627.0	1130.0

gases because the contributions of molecular properties to D^* and K^* are either nearly equal or negligible. Then, since the same initial composition and temperature of the reaction mixture would be used regardless of the scale of the reactor, the invariance of Q_1, and the invariance of Q_2 both imply that $(L/\bar{u})_2 = (L/\bar{u})_1 = t_R$. Thus, for reactions where $K^* = D^*$, $P_1 = P_2$ and the conditions for approximate chemical similarity are the same for both isothermal and adiabatic operation.

Relations like equations 130a and 130b might be obtained for non-adiabatic operation, that is, for a reactor operated with heat transfer. However, this possibility is not particularly interesting. The errors for $s > 0.9$ in the assumption that $\hat{K}(s)$ does not depend on Reynolds number are the same as in the adiabatic case, but here they would have a much greater influence on the attainment of thermal and chemical similarity because of the larger radially-directed heat flux.

The conditions for approximate similarity may also be deduced from the equations for an axial-diffusion model. For example, the paper

of Fan and Bailie (76) cited in Chapter II implies that the invariance of the parameters

$$N_{Pe} = \frac{\bar{u}L}{2\,D_T} \quad \text{and} \quad N_{DI} = \frac{2\,k_{Rn}\,L(C_1^\circ)^{n-1}}{\bar{u}} \tag{131}$$

and the boundary condition, $\gamma = 1$ for $z = 0$ are sufficient conditions for chemical similarity.

Again consider an isothermal reaction proceeding in two reactors operating under conditions of chemical similarity. The production rates differ by a factor of X as in equation 129. The invariance of N_{DI} implies that $(L/\bar{u})_2 = (L/u)_1 = t_R$. From Taylor's equation for the virtual axial diffusivity, equation 22, and the Blasius friction factor equation, it follows that

$$\frac{D_T}{\nu} = N_{Re}^{7/8} \tag{132}$$

This relation, equation 129, definitions 131 and the definition of N_{Re} yield

$$(r_w)_2 = 2^{-3/5}\left(\frac{1}{t_R\nu}\right)^{1/25}\left[X\,(Lr_w^2)_1\right]^{9/25}(N_{Re})^{-8/25} \tag{133}$$

For the prototype of the above example and $X = 0.1$, the conditions for the model are given in Table 11 under Model 2.

Taylor's equation for virtual axial diffusivity is inaccurate for low Reynolds numbers, so the conditions for a model may also be calculated from the graph of $D_T' = D_T/(2r_w\bar{u})$ versus $4f_F$ obtained by Tichacek, Barkelew and Baron (58) from experimental velocity

data. In this case the relationships are

$$(r_w N_{Re})_2 = \frac{2 X (Lr_w^2)_1}{\nu_R} \tag{134a}$$

$$(r_w)_2 = \left[\frac{X(Lr_w^2)_1}{4 N_{Pe} D_T'}\right]^{1/3} \tag{134b}$$

and

$$D_T' = F_1(4f_F) = F_2(N_{Re}) \tag{134c}$$

where F_1 is the graphical relation in Figure 1 of the paper of Tichacek, Barkelew and Baron. The solution of these three simultaneous equations by trial for the prototype described above gives as conditions for the model the entries in Table 11 under Model 3.

The only conclusion to be drawn from these three sets of conditions for approximate similarity is that they are different. It would be interesting to know which set gives conversions at the reactor outlets that are most nearly the same for both model and prototype, but such information was not obtained in this investigation.

Illustrative Calculations

Parametric Sensitivity.--The study by Bilous and Amundson (89) of chemical reactor stability and sensitivity led them to recognize a phenomenon called parametric sensitivity. This term is used to describe the behavior of the solution to the equations of a piston-flow model of a tubular reactor when changes are made in the values of the parameters of the equations or the boundary conditions. In one example, their model shows that only a 2.5°C increase in wall temperature causes the appearance

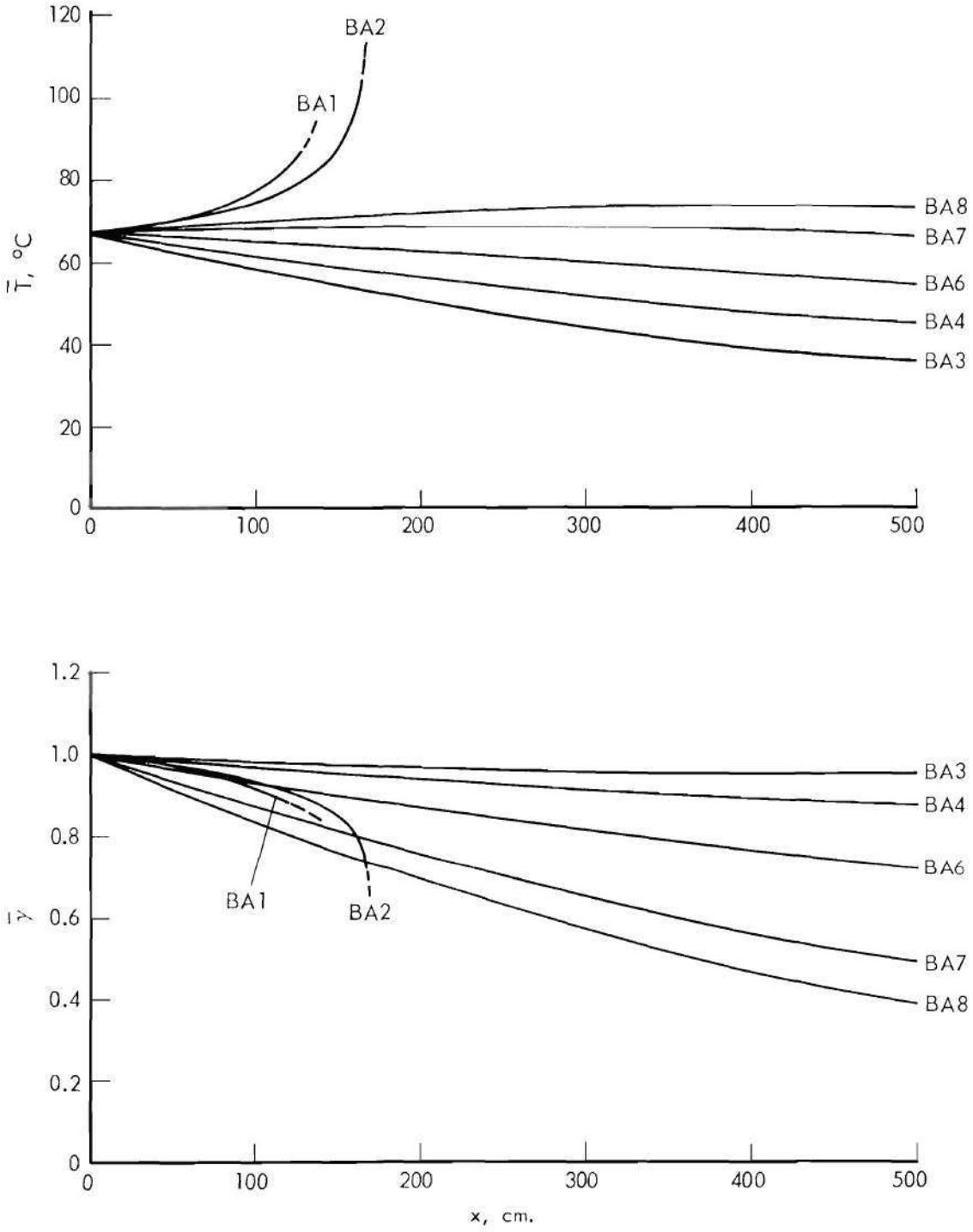

Figure 18. Results of Illustrative Calculations - Parametric Sensitivity.

of a "hot spot" or ignition zone in which the temperature of the reaction mixture increases by 70°C.

Some calculations were performed to see whether the radial-diffusion model of this thesis is also subject to parametric sensitivity and if so, what the effect of distributed rather than lumped parameters might be. The results are presented in Figure 18. The input data were chosen so that the calculations would be comparable to those indicated by Bilous and Amundson in their Figures 1 and 2. These input data are identified in Table 9 by BA1 and BA2, etc.

Thermal Initiation.--Calculations were made to illustrate the use of the mathematical model of this thesis for thermally initiated reactions. The resulting axial profiles of average concentration and temperature are presented in Figures 19a and 19b. The input data for these calculations, including programs of temperature control, are identified in Table 9 by TIX for the exothermic case and TIN for the endothermic case.

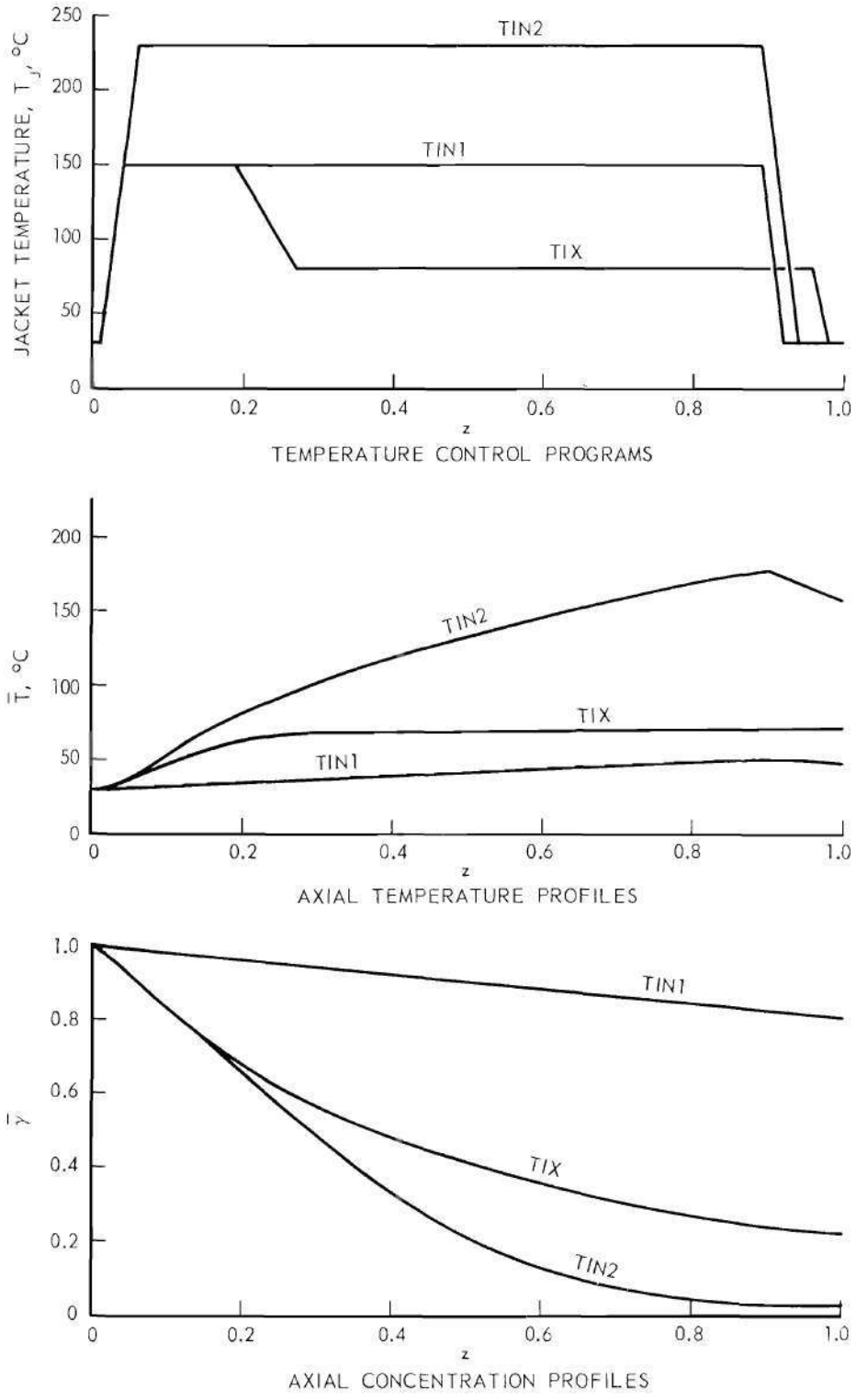

Figure 19. Results of Illustrative Calculations - Thermal Initiation and Programmed Control.

CHAPTER VI

DISCUSSION OF RESULTS

The results presented in this thesis may be divided into two classifications, the results that pertain only to the objectives described in Chapter I and the results that, while essential to this thesis, are also of interest in other contexts. In the first section of this chapter the results that are limited to the objectives of this study are discussed. In the second section, the results that have a wider application are mentioned.

On the Attainment of the Objectives of This Study

The general objective of this study is to provide an improved method for predicting the behavior of those industrial chemical reactions in which there is an important coupling of transport phenomena with chemical reaction. Specifically, this objective is sought for homogeneous reactions in continuous-flow, tubular reactors. The results of this thesis are examined below for progress toward this objective. First, some comments concerning the mathematical model are presented. Then, the results of the experimental and theoretical investigations are examined and compared and the results of the illustrative calculations are discussed.

Comments on the Mathematical Model of This Thesis.--The first assumption of the model described in Chapter III is that variations in the physical properties of the reaction mixture are negligible. Figures 15 and 16

indicate the variation of two important physical properties of the reaction mixtures with temperature and extent of reaction. These data show that substitution of sodium acetate for sodium hydroxide has only a slight effect on the viscosities or densities of imitation reaction mixtures. This indicates that the influence of the extent of reaction on these properties is small. However, as expected, the viscosities and densities of the imitation reaction mixtures were found to be dependent on temperature.

The adequacy of the velocity distribution used in this model was discussed in Chapter III. It may be of interest to note that the shapes of the eddy diffusivity distributions of Figure 9 are more nearly like those of Hinze (68), Reichardt (15), and Page and co-workers (34) than the distributions of Rothfus and co-workers (16) or Corcoran, Opfell, and Sage (51).

In the mathematical model presented in Chapter III it is implicitly assumed that the character of the flow is turbulent. Also, the third stated assumption is that the velocity and diffusivity distributions do not change axially, that is, in the z direction. The experimental velocity data of Figures 5 and 6 show that the flow does have the expected turbulent velocity distribution for isothermal conditions. The experimental data of Figure 6 are slightly below the computed distribution. This condition is caused by the use of the experimental friction factor data of Table 7 rather than friction factors for smooth-walled pipe to convert experimental velocity data to u^+, y^+ coordinates.

Some of the data of Figure 6 were obtained at each of the three test sections. Since the differences between the data from the three

sections is within the experimental error indicated in the figure, the flow is considered to be fully developed, that is, unchanging in the axial direction, for isothermal conditions. The same holds true for the data of Figure 5.

Criticisms of imprecise velocity data made in Chapter II apply equally well to the data of Figures 5 and 6. However, the reader should note that they are not used here to establish eddy diffusivity distributions.

Data concerning the change in velocity distribution caused by heat transfer to a fluid of variable properties are given in Figure 12. The velocity data for flow with heat transfer were obtained in test HT3. From the conditions of this test a value of +0.0029 was calculated for Deissler's heat flux parameter, β_D. The velocity distribution for $\beta_D = +0.002$ in Deissler's (44) Figure 8b and the wall temperature and fluid properties of test HT3 give 1.092 as a prediction of $u_{max}/\bar{u}$. The experimental data of Figure 12 clearly contradict this prediction.

The data of Figure 12 indicate that the effect of heat transfer on the velocity distribution may be regarded as negligible for the purposes of this study. Other data obtained for an inlet Reynolds number of about 5,000 are similar, but less precise. These data have been omitted because they contribute no additional information.

Even though the effect of heat transfer on the velocity distribution of a fluid having variable properties may be negligible, this does not necessarily mean that the effect on the eddy diffusivity distribution is negligible. An immeasurably small change in the velocity distribution in the vicinity of the tube wall could very well change

the velocity gradient by more than 10 per cent in this part of the flow and produce a significant change in the eddy diffusivity of momentum defined by equation 82. Unfortunately, the data of Figure 12 are not sufficiently precise to determine the actual sizes of the effects of heat transfer on the velocity and eddy diffusivity distributions.

Examination of Results.--The comparisons between the experimental and theoretical results of this study are shown in Figures 11, 13, and 14 and in Table 10.

Temperature distributions of tests HT3, HT1, HTS10, and HTS5 are presented in Figures 11a, b, c, and d, respectively. The agreement between the shapes of the experimental and computed temperature distributions in these figures is entirely satisfactory for the purposes of this study. Since accurate values of the external heat transfer coefficient, A_x, were not determined experimentally, the values of A_x used in the calculations of Figures 11a and 11b were chosen to give the best agreement with experimental temperatures. It was found that a change in the value of A_x resulted in a shift of the computed temperature distribution, but very little change in its shape.

The points of Figures 11c and 11d represent Sleicher's (13) experimental data for heat transfer to air flowing in a pipe with a constant wall temperature. The value of A_x in these calculations was chosen large enough to make the difference between the wall and jacket temperatures negligible. Otherwise, the value of A_x had no bearing on these calculations. The deviation of the computed curve in Figure 11d from the experimental distribution is a consequence of inaccuracy in the eddy diffusivity distribution for the central part of

the flow. This was to be expected since the shape of the computed velocity distribution does not agree perfectly with the experimental data for this value of the Reynolds number (Figure 8).

The dashed line in Figure 11b is a temperature distribution predicted from velocity and eddy diffusivity distributions computed using equation 91. The velocity distribution is quite plausible, but the inadequacy of the eddy diffusivity distribution is evident from the figure. In particular, the attention of the reader is directed to the shape of the temperature distribution in the central part of the flow. This shape is evidently due to the fact that the eddy diffusivity obtained from equations 90 and 91 vanishes at $r = 0$.

The agreement between computed and experimental results for chemical reaction tests is not as satisfactory as the agreement for heat transfer tests. Before discussing these, some of the sources of experimental error will be mentioned.

The greatest cause of error in the chemical reaction tests was inadequate control of the flow rates of the three streams comprising the reactor feed. As mentioned in Chapter IV, these flow rates were indicated by rotameters and controlled by manually-operated valves. These flow rates often deviated from the desired values by as much as two or three per cent and occasionally by as much as five to ten per cent. Although the rates were observed and adjusted frequently, they could not be watched continuously, because the efforts of both operators were needed to obtain some of the data of these tests. The number and size of the deviations in the flow rates could have been

reduced by the use of automatic controls or the help of a third operator.

Another feature of this experimental work was the large number of readings needed for a single test. No less than two stop watches, three weighing scales, three burettes, one micrometer head, and a potentiometer were read repetitively during a test. These readings were made as rapidly as practical in order to minimize the expense of the tests due to the consumption of reactants. Under these circumstances, it is not surprising that an occasional erroneous reading was recorded.

Attention must be called to the problem of determining the virtual displacement of a sampling probe. The values of r/r_w for the experimental points shown in Figures 13 a, b, and c and 14a, b, and c were obtained from equations 125c, 126, and 127 by the relation $r/r_w = 1 - \delta_v/r_w$. Formulas analogous to equations 125c and 127 were derived for determining the virtual displacement of an impact pressure probe. However, the values of δ_v computed from these formulas were much less than the experimental values determined by Young and Maas (152) and Macmillan (19). For this reason the virtual displacements for sampling probes given in equations 125c, 126, and 127 are open to question. The values of δ_v estimated by these equations are surely more realistic than $\delta_v = 0$, but no attempt has been made to confirm them experimentally and the reader is warned that they may not be correct. If the sampling flow rate is not excessive, the maximum possible value of δ_v is r_p, which in this thesis is 0.040 inch.

No attempt was made to obtain data points closer to the tube wall than $r/r_w = 0.951$ because of these uncertainties in the determination of y_v and because of the need for a relatively large sampling flow rate when samples were taken for analysis. The data for which $r/r_w = 0.951$ were obtained with the sampling probe halfway withdrawn into its recess in the tube wall, that is, with the probe axis centered at the wall of the reactor tube or $y_o = 0$. It should be noted that the problem of determining the virtual displacement of a sampling probe would have been less if the mouth of the probe had been rectangular in shape instead of circular.

In Table 10, data concerning pseudo-adiabatic chemical reaction tests are presented. Experimental values of the final concentration of the limiting reactant are compared with values computed from the radial-diffusion model of this thesis and the equations for a piston-flow model. There are two anomolous entries in the table, the experimental concentration for test R7A and one of the computed values for R6A. The discrepancy in the final concentrations shown for test R7A is probably due to poor flow control, poor sampling, or an error in analysis during the determination of the mass flow rate of sodium hydroxide at the beginning of the test.

The cause of the disagreement between the two computed values for test R6A is unknown. Presumably, the concentration given by the equation for piston-flow is correct, since the conversion given by a piston-flow model is generally accepted to be the upper limit for conversion in tubular reactors. For first order reactions, the work of Chambré, cited in Chapter II, indicates that this is so. However, the

writer knows of no general proof. The discrepancy between the computed values for test R6A may be due to cumulative discretization or truncation error in the radial-diffusion calculations. In this case the discrepancy could be reduced by the use of a smaller value of (Δz). This was not done, however.

The concentration and temperature distributions obtained in the combined chemical reaction and heat transfer tests are shown in Figures 13a, b, and c and 14a, b, and c.

The shapes of the experimental and computed temperature distributions in Figures 13a, b, and c agree fairly well, except that the data for $z = 1.0$ in Figures 13b and 13c indicate that the change in the temperature gradient near the tube wall is actually more abrupt than the change shown by the computed distribution. Both of the computed temperature distributions in Figure 13a are based on an inlet temperature of 9.0°C, corresponding to the inlet temperature for the experimental data at $z = 1.0$. At the time that the experimental temperatures for $z = 0.36$ were recorded the inlet temperature was 0.6°C greater. This fact explains most of the discrepancy between the computed and experimental temperature distributions for $z = 0.36$. This same situation appears in Figure 13c except that here the experimental inlet temperature for $z = 0.36$ was 0.45°C lower than the inlet temperature for $z = 1.0$.

The concentration distributions of Figures 14a, b, and c are almost as flat as the distributions for the pseudo-adiabatic tests. However, the reaction rate, $R(\gamma, \theta)$, which is almost independent of radius in the pseudo-adiabatic tests, increases with increasing radius

and reaches a sharp maximum near the tube wall. This behavior is due to the temperature distribution, of course.

The agreement between the computed concentration distributions and experimental data in Figures 14a, b, and c is as good as or better than the agreement found for the pseudo-adiabatic tests. The discrepancies between the shapes of the computed and experimental distributions are certainly well within experimental error.

Examination of the Results of Illustrative Calculations.--The results of illustrative calculations concerning parametric sensitivity and thermal initiation are shown in Figures 18 and 19. The comparison of conditions for approximate chemical similarity requires no further discussion, since the only object was to show that the predictions obtained from the radial-diffusion and axial-diffusion models are different.

The series of curves in Figure 18 show that the radial-diffusion model of this thesis is indeed subject to parametric sensitivity. For example, compare the curves identified by BA2 and BA3. The input data, shown in Table 9, were exactly the same, except for the velocity which was 200 cm./sec. for BA3 compared to 100 cm./sec. for BA2. The difference in the results of the two calculations is attributed to greater values of eddy diffusivity, resulting in more effective heat removal in BA3.

The cumulative error in the scheme of numerical analysis described in this thesis is dependent on the value chosen for (Δx), all other things being the same. This can be seen by comparing the curves for BA1 and BA2. The only difference in the sets of input data for these

two is the value of L. Since the same value of (Δz) was used in both calculations, the result of a change in L is a change in (Δx), the difference in the axial displacements for two consecutive steps in the computation. Here, the values of (Δx) are 20 cm. and 5 cm. for BA1 and BA2, respectively.

The calculations identified by BA1 and BA2 also reveal the magnitudes of stepwise changes in the dependent variables that can be tolerated by the numerical method without trouble. The solid lines in Figure 18 indicate computed values. For BA1 and BA2 the lines end when the absolute value of $(\Delta\gamma)$ per step has increased to about 0.04. The curves are terminated at these points because after the last computed point, the differences between successive values of the elements of $\vec{\gamma}$ did not become small as the number of iterations increased. In all probability, this behavior was due to one or more of the γ_i's that are elements of $\vec{\gamma}$ becoming negative. At the last computed points, the number of iterations for BA1 and BA3 were 7 and 19, respectively. Ordinarily, the number of iterations should not exceed 4.

The behavior of the radial-diffusion model in calculations BA1 and BA2 illustrates a weakness of the scheme of numerical analysis used in this investigation. The use of a constant value of (Δz) throughout a calculation is disadvantageous if the partial derivatives of γ or θ with respect to z become large. Suppose that the value chosen for (Δz) is small enough to allow the calculation to proceed in intervals where the partial derivatives with respect to z are large. Then, if the value of (Δs) is constant, it will be wastefully small throughout

the rest of the calculation. In this respect the Runge-Kutta method might prove to be superior to the backward difference formula for integrating equation 111 because of the ease with which (Δz) can be changed between steps in the computation.

The illustrative calculations concerning thermal initiation of chemical reaction are presented in Figure 19. Calculation TIX, which shows the use of preheat and reaction sections of a tubular reactor for an exothermic reaction, is not particularly noteworthy except that it shows the kind of calculations for programmed temperature control that can be carried out by the methods of this thesis. Calculation TIN2 shows that the starting material is about 35 per cent converted at the value of z where the temperature has reached only 80°C. This fact is an indication that the reaction rate is much more rapid near the hot wall than in the central part of the stream. Murdoch and Holland (86) and Perkins and Rase (86) consider endothermic reactions in tubular reactors with preheat sections. By the definitions of preheat section used in these papers, the length of a preheat section is such that very little conversion, say one per cent, takes place in this section. However, the calculations shown in Figure 19 indicate that the amount of heating done in a preheat section defined in this way would also be very small. For example, the average temperature of the reaction mixture in TIN2 has increased less than 5°C at the point where the conversion has reached 5 per cent.

Other Results of Interest

Several results were obtained as byproducts of this investigation. Perhaps the most useful of these is the velocity correlation developed in Chapter III. An improved choice of φ in equation 96, guided by precise experimental data, should lead to a truly accurate correlation of the distribution of the temporal-mean velocity for flow in pipes.

An application of regression analysis to the calculation of eddy diffusivities of momentum from velocity data is presented in Appendix I. It is hoped that this presentation will allow calculations and discussions concerning eddy diffusivities to be put on a more objective basis.

The experimental data of Figure 12 indicate the inadequecy of the only existing method of predicting the effect of heat transfer on the velocity distribution of a fluid having variable properties.

Finally, the temperature distribution obtained using equation 91 and shown in Figure 11b indicates the consequences of using velocity distributions for which the eddy diffusivity vanishes at $r = 0$. It is concluded from this result that either ε_v is significantly greater than zero at $r = 0$ or the ratio $\varepsilon_H / \varepsilon_v$ increases without bound as r approaches zero.

CHAPTER VII

CONCLUSIONS

The published studies that are most closely related to this one are those of Chambré (100) and Cleland and Wilhelm (98). The main differences between this study and the work of Chambré are the inclusion of distributed radial diffusivities in the mathematical model of the present study, the inclusion of numerical and experimental results, and the use of different methods of obtaining approximate solutions. This study differs from that of Cleland and Wilhelm by employing turbulent rather than laminar flow and by considering non-first-order reactions and the presence of heat transfer and an appreciable heat of reaction as well as first-order, isothermal reactions. The main difference between the experimental investigation of this study and the one of Cleland and Wilhelm is that the measurements show the radial distribution of concentrations and temperatures instead of the bulk values of these variables.

In Chapter II, seven criteria of merit were listed for velocity correlations. The isothermal velocity distributions computed by the mathematical model of this investigation satisfy the last six of these criteria for values of Reynolds number from 3,000 to 50,000. According to the first criterion, that is, lack of conflict with experimental data, the computed velocity distributions are judged good at Reynolds numbers of 5,000, 10,000, and 19,500 and fair at a Reynolds number of 39,500.

Temperature distributions were computed for two of the heat transfer tests of this study and two tests made by Sleicher. The shapes of the computed distributions are in good agreement with the experimental data of these tests.

The data obtained in the tests with chemical reaction and pseudo-adiabatic conditions reveal that the temperatures and concentrations at cross sections perpendicular to the direction of flow are almost independent of radius throughout most of the cross-sectional area. In view of this, it is not surprising that for these tests the mathematical model used in this study has no advantage over a piston-flow model. On the other hand, the validity of the mathematical model of this study is supported by a three-way comparison of experimental data and outlet concentrations computed using the equations of a piston-flow model and the present radial-diffusion model.

In the tests with chemical reaction and heat transfer, the radial concentration gradients were found to be small in the region where concentrations could be measured. However, the possibility of developing appreciable radial temperature gradients was demonstrated. Hence, comparisons with these data provide a severer measure of the accuracy of the mathematical model than comparisons with the pseudo-adiabatic data. Comparisons of data with the velocity and temperature distributions computed for the tests combining chemical reaction and heat transfer show agreement within the accuracy of the experimental measurements.

The relatively simple method of numerical analysis used in the theoretical part of this study gave surprisingly good results.

However, the slight disagreement between the final concentrations computed for Test R6A and the need for the adjustment of the value of (Δz) during computation call for further work on this part of the problem.

The illustrative calculations show that the radial-diffusion model of this study is subject to parametric sensitivity in certain regions. The model yields different conditions for approximate chemical similarity than do axial-diffusion models. The assumptions of earlier methods of calculation for endothermic reactions in tubular reactors with preheat sections are shown to be questionable.

The objective of this study was largely, but not fully, attained. The radial-diffusion model and the method of numerical analysis presented here are believed to need further development before they will be satisfactory for routine design calculations. However, the results of this combination of mathematical model and numerical method are believed to be sufficiently valid to justify the use of the combination in its present state as a research tool.

APPENDICES

APPENDIX I

ON THE ESTIMATION OF EDDY DIFFUSIVITIES

Discussion.--The appendix concerns the estimation of values of eddy diffusivities from discrete data. The calculation of values of eddy diffusivity of momentum, heat, or mass by means of equation 6 or other analogous formulas requires values of derivatives of velocity, temperature, or concentration with respect to displacement. However, only values of the variables themselves have been measured experimentally, so the calculation of values of eddy diffusivities involves the estimation of derivatives from these data.

The difficulties in estimating eddy diffusivities from experimental data were mentioned as early as 1939 by Sherwood and Woertz (33) and more recently by Lykoudis (169), and Hefner (50). The fundamental cause of difficulty is the fact that the experimental measurements do not represent just the relationship between two variables, but include experimental error from many sources.

At least four methods may be used for computing derivatives from discrete, error-containing data. All of these involve, in some form or another, an alteration of the original data to remove the general irregularity that is attributable to experimental error. Such an alteration is called "smoothing." It is interesting to note that there is a theoretical justification for the use of smoothing in combination with

differentiation. Such a justification is given by Miller (170) in a discussion of Whittaker's "cardinal function."

In the least sophisticated of the four methods for estimating derivatives, the original data are represented by a table or graph. If the data are tabular, they are smoothed by a numerical formula; if graphical, they may be smoothed "by eye." Then, standard numerical or graphical methods are employed to estimate derivatives from the smoothed data.

The second method involves what Lanczos (171) terms "smoothing in the small," because the data are correlated and smoothed locally. This method consists of making a least squares fit of some low-degree polynomial to an arbitrary number of adjacent data points. Alternatively, the data for which the values of the independent variable lie within an arbitrary interval may be represented by some low-degree polynomial.

The third method is described by Lanczos (172) as "smoothing in the large." In this the original data are represented by a Fourier series or an orthogonal polynomial series. Smoothing is effected by examining the coefficients of the series and truncating it at the point where the successive coefficients no longer decrease, but begin varying irregularly. The differentiation of this truncated series gives the required estimates of derivatives.

The fourth method is also described by Lanczos (173). He shows that

$$\frac{df(x)}{dx} = \frac{3}{2\varepsilon^3} \int_{-\varepsilon}^{\varepsilon} tf(x+t)dt - \frac{1}{10} \varepsilon^2 \frac{d^3 f}{dx^3} + \ldots$$

The integral on the right hand side may be evaluated by a quadrature formula or an algorithm described by Lanczos.

Frequently, the estimate of a derivative of a function gives only part of the information that is needed. Suppose that two comparable sets of experimental data are available for some interval of the independent variable and that these sets yield different estimates of derivatives throughout part of this interval. In this situation, one would like to answer two questions: Is the difference in the estimates only an apparent difference due to the variability of the data, or is it a real difference in the measured phenomena? How reliable are estimates obtained from one set of data compared to those for the other set? To answer these questions, one needs to have not only estimates of the values of the derivative, but also an estimate of the variability of these values. In other situations the estimation of variability gives one kind of a quantitative measure of the quality of a set of data. Among the four methods for the estimation of the values of derivatives, only the second is used easily for the estimation of variability.

Whitaker and Pigford (174) consider the estimation of the values of derivatives and their variability. They present formulas based on a least-squares fit of a second-degree polynomial to five, successive, uniformly-spaced data points. They point out that "One of the assumptions involved in fitting a least squares curve to some experimental data is that the function chosen to fit the data is in fact the true functional relationship between y and x. . . .In most cases where curves are fitted to experimental data the true functional relationship is

unknown and the standard deviation is made up of the error of the original data and the error caused by the choice of an improper function to correlate the data." The formulas of Whitaker and Pigford, while useful for uniformly spaced data, have three deficiencies in addition to the one mentioned just above. Obviously they can not apply to the general case where the data are not uniformly spaced. These formulas do not allow for the inclusion of independent, repeated measurements, so that at least part of the information available from such measurements is wasted. Finally, there are occasions when it is desirable to fit a second-degree polynomial for an interval larger than one including five adjacent data points. Also, of course, the number of points may vary, for example, due to the apparent curvature indicated by the data.

Regression analysis appears to be a more general method for obtaining estimates of the values of a derivative and their variability than the method described by Whitaker and Pigford. The reader is referred to the book of Bennett and Franklin (175) for a detailed presentation of this standard method of statistical analysis. The error introduced in representing an arbitrary function by a polynomial of low degree rarely causes any practical difficulty, because the usual limitation to the degree of the regression polynomial is the number of coefficients that can be demonstrated to be significantly different from zero. The technique of variance analysis used to test the significance of the coefficients may be found in the book of Bennett and Franklin.

Analysis.--The effect of an inaccurate functional representation may also be examined in another way. This will be illustrated for linear regression. In the following analysis, random variables will be assumed

to be normally distributed. Distribution-free regression is described by Mood (176), and it may be possible to account for the error of inaccurate functional representation in this case, also.

It is assumed that w, a continuous function of x, exists and has continuous first and second derivatives in some interval $a \leq x \leq b$. Within this interval, w may be expressed by a Taylor series with remainder,

$$w(x) = w(x_o) + z\, w'(x_o) + \frac{z^2}{2} w''(x_o + \theta z) \qquad (135)$$

where $z = x - x_o$ and $0 < \theta < 1$. The experimentally measured variable Y can be written

$$Y_i = w(x_i) + y_i) \qquad (136)$$

where the random variables y_i are assumed to be independently, normally distributed with means of zero and a common variance of σ^2. The variable Y has an expected value $\tilde{Y}_i = w(x_i)$, and a variance of σ^2 about $\tilde{Y}_i$.

The problem is the estimation of $w(x_o)$ and $w'(x_o)$ from a set of experimental data: (Y_i, x_i), $i = 1, 2, \ldots, n$. The combination of equations 135 and 136 gives

$$Y_i = w(x_o) + z_i w'(x_o) + \frac{z_i^2 p_i}{2} + y_i \qquad (137)$$

where $p_i = w''(x_o + \theta_i z_i)$. Since y_i is unknown, the random variables A_i and B_i are introduced by

$$A_i + z_i B_i = w(x_o) + z_i w'(x_o) + y_i \qquad (138)$$

The expected values of A_i and B_i are $\tilde{A} = w(x_o)$ and $\tilde{B} = w'(x_o)$, respectively. The constants $\tilde{A}$ and $\tilde{B}$ are estimated by the method of least squares. The quantity to be minimized is

$$Q = \sum_{i=1}^{n} \left(Y_i - a - z_i b - \frac{z_i^2 p_i}{2} \right)^2 \tag{139}$$

where a and b are estimates of $\tilde{A}$ and $\tilde{B}$. The partial derivatives of Q with respect to a and b are set equal to zero and the resulting equations give

$$b = \frac{n \Sigma Y_i z_i - (\Sigma z_i)(\Sigma Y_i) - \frac{n}{2} \Sigma z_i^3 p_i + (\Sigma z_i)(\Sigma z_i^2 p_i)}{n \Sigma z_i^2 - (\Sigma z_i)^2} \tag{140}$$

$$a = \frac{\Sigma Y_i - b \Sigma z_i - \frac{1}{2} \Sigma z_i^2 p_i}{n} \tag{141}$$

The sample estimate of $\tilde{Y}$ can be written

$$\underline{Y}_i = a + b z_i + \frac{z_i^2 p_i}{2}$$

and the corresponding sample variance of b is

$$\text{var}(b) = \frac{\sum_{i=1}^{n} (Y_i - \underline{Y}_i)^2}{(n - 2) \Sigma z_i^2} \tag{142}$$

In order to see the effect of terms involving p in equation 142, let

$$a^* = \frac{\Sigma Y_i - b \Sigma z_i}{n} \tag{143}$$

$$b^* = \frac{n \Sigma Y_i z_i - (\Sigma z_i)(\Sigma Y_i)}{n \Sigma z_i^2 - (\Sigma z_i)^2} \tag{144}$$

$$Y_i^* = a^* + b^* z_i \tag{145}$$

and $$\text{var}^*(b) = \frac{\Sigma (Y_i - Y_i^*)^2}{(n-2)\ \Sigma z_i^2} \tag{146}$$

Then,

$$\underline{Y}_i = Y_i^* + z\, E_b + \frac{n-1}{2n} z_i^2 p_i \tag{147}$$

where

$$E_b = b - b^* = \frac{-\frac{n}{2} \Sigma z_i^3 p_i^2 + (\Sigma z_i)(\Sigma z_i^2 p_i)}{n \Sigma z_i^2 - (\Sigma z_i)^2} \tag{148}$$

Also let

$$E_v = \text{var}(b) - \text{var}^*(b)$$

$$= \frac{\Sigma 2(Y_i - Y_i^*)(zE_b + \frac{n-1}{2n} z_i^2 p_i) + (zE_b + \frac{n-1}{2n} z_i^2 p_i)^2}{(n-2)\ \Sigma z_i^2} \tag{149}$$

The usual equations for linear regression analysis are 143 through 146. The error introduced by using these equations for a non-linear function, $w(x)$, is given by the term containing p in equation 141 and by equations 148 and 149.

The choice of x_o has an influence on E_b. For example, suppose that the p_i are all equal. This condition might be approximated by making the interval (x_o, x_n) small, provided that there were still enough data to justify the application of statistical methods. For the purpose of illustration, also suppose that the spacing of the z_i is uniform. Then $x_o = \bar{x}$ causes E_b to vanish, because $z_i + z_{n-i+1} = 0$ and $z_i^3 + z_{n-i+1}^3 = 0$ for $i \leq n/2$.

If $w(x)$ is linear, equation 146 shows that the variance of b may be reduced by spreading the data over as large an interval of x as possible. However, the presence of the z^2 and z^4 terms in the numerator of equation 149 shows that an increase in Σz^2 obtained by enlarging the interval may increase the error of the variance estimate.

An Application.--The use of regression equations in estimating values and variability of eddy diffusivity of momentum will be demonstrated by a consideration of Sleicher's data for the flow of air through a smooth-walled pipe. Three sets of these data were available for Reynolds numbers of 39,000, 39,100, and 40,000. When these three data sets were combined, the unusually large total of 77 experimental values of velocity were available over a narrow range of Reynolds number. There is an effect of Reynolds number on the dimensionless velocity u^+ for a fixed y^+, but this effect is not known quantitatively. So, limiting the range of Reynolds number eliminates one known source of variability in the data.

All of the data were first transformed to the variables u^+ and $\log y^+$ because the relationship between these variables appears roughly linear, at least within small intervals of $\log y^+$. Then, three intervals, $\log 50 \leq \log y^+ \leq \log 100$, $\log 100 \leq \log y^+ \leq \log 500$ and $\log 300 \leq \log y^+ \leq \log 900$ were selected. Estimates of the regression coefficients $\tilde{A}$ and $\tilde{B}$ in

$$u^+ = \tilde{A} + \tilde{B} \log y^+$$

were made for the data in each of these intervals. No attempt was made to estimate the errors shown in equations 148 and 149, but these were

restricted by choosing $(\log y^+)_o = \overline{\log y^+}$, limiting the size of the intervals of $\log y^+$, and choosing each interval so that $d^2u^+/[d(\log y^+)^2]$ appeared to have the same sign throughout most of the interval. It is possible that the estimate of the coefficient $\tilde{C}$ in

$$u^+ = \tilde{A} + \tilde{B} \log y^+ + \tilde{C}(\log y^+)^2$$

would be found significantly different from zero for the interval $\log 300 \leq \log y^+ \leq \log 900$. This possibility was not tested, but if it were true, the variability due to error would have been reduced.

Not all of Sleicher's data were tabulated in terms of the variables u^+ and y^+. In the process of transforming the original u-y data to u^+ and y^+, an inconsistency was found between the tabulated values of u^+ and y^+_{max} for data at a Reynolds number of 40,000. A value of f_F was calculated from Sleicher's tabulated y^+_{max} value and this value of f_F was used to convert all of the u-y data of this set to the u^+-y^+ form. The computed values of u^+ corresponding to values of y^+ less than 240 did not agree with Sleicher's table for $N_{Re} = 40{,}000$, but the resulting values of u^+ gave better agreement with the other two sets of data than the original tabulated values of u^+.

Other than the points just mentioned, the calculations were entirely straightforward. They are shown below for the interval $\log 30 \leq \log y^+ \leq \log 100$.

$$n = 12, \quad \Sigma u^+ = 181.8, \quad \Sigma \log y^+ = 21.93872,$$

$$\Sigma (u^+)^2 = 2759.56, \quad \Sigma (\log y^+)^2 = 40.288067,$$

$$\Sigma\, u^+(\log y^+) = 333.319871$$

$$\text{Est.}\ \frac{du^+}{d(\log y^+)} = b = \frac{11.37916}{2.15753} = 5.27416$$

$$\text{Est.}(u^+)_{\overline{\log y^+}} = a = \frac{66.09168}{12} = 5.50764$$

$$\text{var}(u^+) = \frac{\Sigma\,(u_i^+ - a - b \log y_i^+)^2}{n - 2} = \frac{0.289}{12 - 2} = 0.0289$$

$$\text{var}(b) = \frac{\text{var}(u^+)}{\Sigma\,(\log y^+)^2 - \frac{1}{n}\,(\Sigma \log y^+)^2} = \frac{0.0289}{.179} = 0.161$$

$$\frac{du^+}{dy^+} = \frac{1}{y^+ \ln 10}\,\frac{du^+}{d(\log y^+)} = \frac{5.27416}{(67.42)(2.303)} = 0.0340$$

Since for $w = f(u, v)$

$$\text{var}(w) = \left(\frac{\partial f}{\partial u}\right)^2 \text{var}(u) + \left(\frac{\partial f}{\partial v}\right)^2 \text{var}(v)$$

the variance of du^+/dy^+ is estimated by

$$\text{var}\left(\frac{du^+}{dy^+}\right) = \frac{\text{var}(b)}{(\ln 10)^2 (y^+)^2} = \frac{0.161}{(2.303)^2 (67.42)^2} = 5.70 \times 10^{-6}$$

$$\text{std. dev.}\left(\frac{du^+}{dy^+}\right) = 2.59 \times 10^{-3}$$

Also, from

$$\frac{\varepsilon_v}{v} = \frac{\frac{\tau}{\tau_w}}{\frac{du^+}{dy^+}} - 1$$

$$\frac{\varepsilon_v}{\nu} = \frac{0.936}{0.0340} - 1 = 26.54$$

and an estimate of the variance of ε_v / ν is given by

$$\text{var}\left(\frac{\varepsilon_v}{\nu}\right) \doteq \frac{[(y^+)(r/r_w)(\ln 10)]^2}{b^4} \text{var}(b)$$

$$= \frac{[(67.42)(0.936)(2.303)]^2}{(5.2742)^4} (0.161)$$

$$= 4.40$$

$$\text{std. dev.} (\varepsilon_v / \nu) \doteq 2.10$$

The length of the $100\ (1 - \alpha)$ per cent confidence intervals corresponding to the estimated standard deviations of du^+/dy^+ and ε_v / ν are given by

$$2\ t_{n-2,\alpha} \sqrt{\text{var}\left(\frac{du^+}{dy^+}\right)} \quad \text{and} \quad 2\ t_{n-2,\alpha} \sqrt{\text{var}\left(\frac{\varepsilon_v}{\nu}\right)},$$

respectively, where t is obtained from tables of the Student's t distribution.

All of the results for the three chosen intervals of $\log y^+$ have been summarized in Table 1.

APPENDIX II

A COMPUTER PROGRAM

For the sake of completeness, the computer program actually used in this study is reproduced here. However, it is expected that few potential users of the mathematical model of this thesis will want to use the same computer program, either because their problem is different or because they wish to improve on the method of numerical analysis. The program given below is written for the Burroughs 220 computer and is written in the Burroughs dialect (177) of ALGOL 58 (178). This is a running, de-bugged, program, but not a polished one. An experienced programmer should be able to make a number of improvements. The only essential parts of the program that are omitted here are the statements controlling the formats of the computer outputs. These are not included because of differences in computer hardware and interests of users would prevent them from being widely applicable.

The program consists of a section of definition statements or declarations, three subroutines, a master program, and four subprograms or segments, in that order. The statements governing the reading of the input data appear at the beginning and end of the master program and at the beginning and end of Segment Three.

The attention of the prospective user is directed to two of the eccentricities of this program. The first is the fact that the values of some of the compoenets of the arrays that are part of the outputs from Segments One and Two are meaningless. That is, they are

neither assigned nor used in the program. These components are W(1, 3), V(20, 1), and V(20, 2) at the end of Segment One and W(1, 1) at the end of Segment Two. The second eccentricity is that some of the program variables are used with different meanings in different parts of the program in order to conserve computer memory locations. For example, W(, 3) represents ℓ_p / r_w in one part of Segment One and is used as an error indicator in Segment Three.

In order to keep the program from being completely incomprehensible, the program variables appearing in the inputs and outputs are translated into the nomenclature of this thesis in a supplementary table.

```
COMMENT COMPUTATIONS FOR CHEMICAL REACTIONS IN A TUBULAR REACTOR
WITH HEAT TRANSFER;
COMMENT DECLARATIONS; INTEGER I, I1, I2, I3, I4, N1, N2, N3, N4,
J, J1(), ORD; BOOLEAN Q,S(); ARRAY U(38), RAD(20), V(39,4), W(40,3),
R(38,3), VW(3,3), B(31), DELTJ(10), A(38,3), J1(10), Z1(10), Z2(10),
S(4); FUNCTION RATE1(C,T) = B(9).C.EXP(B(1) - 1.0/T); FUNCTION RATE2(C,
T) = B(9).B(9).C.(C+B(8)).EXP(B(1) - 1.0/T); FUNCTION RATE3(C,T) =
B(12).(C*B(10)).((C+B(8))*B(11)).EXP(B(1) - 1.0/T); FUNCTION DR1(C,T) =
B(9).EXP(B(1) - 1.0/T); FUNCTION DR2(C,T) = B(9).B(9).(2.0.C + B(8)).
EXP(B(1) - 1.0/T); FUNCTION DR3(C,T) = (((B(10)+B(11)).C + B(10).
B(8))/C.(C+B(8))).RATE3(C,T);
COMMENT THIS SUBROUTINE COMPUTES THE RATE VECTOR, R(,N1), FROM
V(,N1).N1 MUST BE SPECIFIED.; SUBROUTINE RVEC; BEGIN  SWITCH ORD,(RP1,
RP2,RP3,RP4); RP1..  FOR I = (1,1,19); BEGIN  R(I,N1) = B(2).RATE1
(V(I,N1),V(I+19,N1)); R(I+19,N1) = B(5).R(I,N1)/B(2)  END;  RETURN;
RP2..  FOR I = (1,1,19); BEGIN  R(I,N1) = B(2).RATE2(V(I,N1),V(I+19,N1));
R(I+19,N1) = B(5).R(I,N1)/B(2)  END;  RETURN; RP3..  FOR I = (1,1,19);
BEGIN  R(I,N1) = B(2).RATE3(V(I,N1),V(I+19,N1)); R(I+19,N1) = B(5).
R(I,N1)/B(2)  END;  RETURN; RP4..  FOR I = (1,1,38); R(I,N1) = 0.0;
RETURN  END RVEC;
COMMENT THIS PROCEDURE GIVES A BULK-FLOW AVERAGE FOR VARIABLES
THAT ARE FUNCTIONS OF RADIUS; PROCEDURE FLOAV(N1,W(,),U(),RAD();C,T);
BEGIN INTEGER I1,I2,N1; FOR I2 = 0,19; BEGIN X1 = RAD(2).U(2).W(2+I2,N1).
```

```
(0.1); FOR I1 = 3,5,7; X1 = X1 + (6.6666667**-2).(RAD(I1-1).U(I1-1).
W(I1+I2-1,N1) + (4.0).RAD(I1).U(I1).W(I1+I2,N1) + RAD(I1+1).U(I1+1).
W(I1+I2+1,N1)); FOR I1 = (9,2,17); X1 = X1 + (1.6666667**-2).(RAD(I1-1).
U(I1-1).W(I1+I2-1,N1) + (4.0).RAD(I1).U(I1).W(I1+I2,N1) + RAD(I1+1).
U(I1+1).W(I1+I2+1,N1)); X1 = X1 + (1.6666667**-2).(RAD(18).U(18).W(18+I2,
N1) + (4.0).RAD(19).U(19).W(19+I2,N1)); IF  I2 EQL 0; C = X1; IF I2 EQL
19; T = X1  END;  RETURN  END FLOAV();
```

COMMENT THIS SUBROUTINE COMPUTES VW(1,N4) AND VW(2,N4) FROM V(,N1), VW(1,N2), VW(2,N2) AND VW(3,N3) VIA NEWTONS METHOD. N1,N2,N3, AND N4 MUST BE SPECIFIED.;

```
SUBROUTINE NEWT; BEGIN  J1(4) = 1; X8 = 3200.0.B(3).B(21);
X9 = 1600.0.B(4).B(22).(2.0 + B(6).0.050625); ORIGN.. EITHER IF ORD EQL 1;
BEGIN  X1 = RATE1(VW(1,N2),VW(2,N2)); X5 = DRI(VW(1,N2),VW(2,N2))  END;
OR  IF ORD EQL 2;  BEGIN  X1 = RATE2(VW(1,N2),VW(2,N2)); X5 = DR2(VW(1,
N2,  VW(2,N2))  END; OR  IF ORD EQL 3;  BEGIN  X1 = RATE3(VW(1,N2),
VW(2,N2));  X5 = DR3(VW(1,N2),VW(2,N2))  END;  OTHERWISE BEGIN  X1 = 0.0;
X5 = 0.0  END;  X6 = (X8.(V(19,N1) - VW(1,N2)) - B(2).X1); X7 = 1600.0.B(4).
B(22).(2.0.V(38,N1) - (2.0 + 0.050625.B(6)).VW(2,N2) + 0.050625.B(6).
VW(3,N3)) - B(5).X1;  X2 = (X8 + B(2).X5)((B(5).X1/VW(2,N2).VW(2,N2)) +
X9) - B(2).B(5).X1.X5/VW(2,N2).VW(2,N2);  IF ABS(X2)  LSS B(15);  BEGIN
N1 = 1;  GO TO BOSS4  END;  X3 = (X6.((B(5).X1/VW(2,N2).VW(2,N2)) +
X9) - (X7.X1.B(2)/VW(2,N2).VW(2,N2)))/X2;  X4 = (X7.(X8 + B(2).X5) -
X6.B(5).X5)/X2; VW(1,N2) = VW(1,N2) + X3; VW(2,N2) = VW(2,N2) + X4;
J1(4) = J1(4) + 1;  IF  (ABS(X3) GEQ B(13)) OR (ABS(X4) GEQ B(14));
GO TO ORIGN; VW(1,N4) = VW(1,N2); VW(2,N4) = VW(2,N2);  RETURN  END
NEWT;
```

```
COMMENT MASTER PROGRAM; TRANS.. READ(;;DATA1); OVERLAY ONE; GO TO
ORIG1; BOSS2.. OVERLAY TWO; GO TO ORIG2; BOSS3.. OVERLAY THREE; GO TO
ORIG3; BOSS4.. OVERLAY FOUR; GO TO ORIG4; INPUT DATA1(FOR I = 19,(20,1,
26); B(I),J1(5),J1(6),K,S(1),S(2),S(3),S(4));

SEGMENT ONE; BEGIN; COMMENT SEGMENT ONE GENERATES THE RADIUS VECTOR;
RAD, THE VELOCITY VECTOR, U, THE EDDY DIFFUSIVITIES OF MASS AND HEAT, AND
THEIR RADIAL DERIVATIVES: ORIG1.. B(18) = 2.0.B(19).B(23)/B(20); B(29) =
0.079.(B(18)*-0.25); B(27) = 5.128 - 0.15808.LOG(B(18)) - 1.52**7.(B(18)*-
2.097); B(28) = 1.45 + 59.305.(B(18)*-0.5163); B(30) = 1.0/(0.175 +
9.508.(B(18)*-0.6266)); WRITE(;;DATA2,LIST2); RAD(1) = 0.0; FOR I =
(2,1,8); RAD(I) = RAD(I-1) + 0.1; FOR I = (9,1,20); RAD(I) = RAD(I-1) +
0.025;

COMMENT COMPUTE U; X2 = 0.0125/J1(5); I2 = J1(5); W(1,1) = 0.0;
X1 = 0.0; W(1,2) = 0.25.B(18).B(29); FOR I = (1,1,19); BEGIN  IF I EQL
13; BEGIN  X2 = 0.050/J1(6); I2 = J1(6)  END; FOR I1 = (1,1,I2); BEGIN
W(2,1) = W(1,1) + X2; W(3,1) = W(2,1) + X2; FOR J = 2,3; W(J,2) = 0.5.
B(18).B(29).(1.0 - W(J,1))/(1.0 + SQRT(1.0 + 0.5.B(29.((B(18).B(27).
(W(J,1)*B(28)).EXP(-B(30).W(J,1)))*2.0))); X1 = X1 + (W(1,2) + 4.0.
W(2,2) +                W(3,2)).X2/3.0; W(1,2) = W(3,2); W(1,1) = W(3,1)
END; U(20-I) = X1; U(39-I) = X1  END;

COMMENT COMPUTE EDDY DIFFUSIVITIES, RADIAL DERIVATIVES OF E.D.,
AND MIXING LENGTHS; FOR I = (1,1,20); BEGIN  X1 = 1.0 - RAD(I);
X2 = B(27).(X1*B(28)).EXP(-X1.B(30)); X3 = SQRT(1.0 + 0.5.B(29).B(18).
B(18).X2.X2);  IF I NEQ 1; W(I,3) = X2/SQRT(RAD(I)); W(I,1) = B(21) +
```

```
0.5.B(25).B(20).(X3 - 1.0); W(I,2) = B(22) + 0.5.B(26).B(20).(X3 - 1.0)
END; X5 = 0.050; FOR I = (1,1,19); BEGIN   IF I EQL 8; X5 = 0.0125;
X1 = RAD(I) + X5; X2 = 1.0 - X1; X3 = B(27).(X2*B(28)).EXP(-X2.B(30));
X4 = SQRT(1.0 + 0.5.B(29).B(18).B(18).X3.X3); V(I,1) = X1(B(21) + 0.5.
B(25).B(20).(X4 - 1.0)); V(I,2) = X1(B(22) + 0.5.B(26).B(20).(X4 - 1.0))
END; X1 = 0.0; X2 = 0.0; FOR I = (1,1,20);  BEGIN   X1 = MAX(X1,W(I,1));
X2 = MAX(X2,W(I,2)) END; B(16) = X1; B(17) = X2; FOR I = (1,1,20);
BEGIN   W(I,1) = W(I,1)/X1; W(I,2) = W(I,2)/X2; V(I,1) = V(I,1)/X1;
V(I,2) = V(I,2)/X2 END; B(21) = B(21)/X1; B(22) = B(22)/X2; B(3) =
X1.B(24)/B(19).B(23).B(23); B(4) = X2.B(24)/B(19).B(23).B(23); IF S(1);
BEGIN   X1 = SQRT(0.5.B(29)); X2 = 0.5.B(18).X1; WRITE(;;ANS1,FORM1) END;
IF S(2); GO TO TRANS; GO TO BOSS2; OUTPUT  DATA2(FOR I = (18,1,30);
(I,B(I)),J1(5),J1(6),K); OUTPUT ANS1(FOR I = (1,1,19);(RAD(I),U(I),
(1.0-RAD(I)).X2,U(I)/X1),B(16),B(17),B(3),B(4),FOR I = (1,1,20);
(RAD(I),W(I,3),B(16).W(I,1),B(16).V(I,1),B(17).W(I,2),B(17).V(I,2)))
END ONE;
```

SEGMENT TWO; BEGIN COMMENT FORMATION OF MATRIX A; ORIG2.. A(1,1) = 0.0; A(20,1) = 0.0; X2 = B(3); I = 1; FOR I2 = 0,19; BEGIN IF I2 EQL 19; BEGIN X2 = B(4); I = 2 END; X1 = 0.1; FOR I1 = (1,1,19); BEGIN EITHER IF I1 EQL 8; BEGIN X1 = 0.025; N1 = 3 END; OR IF I1 EQL 1; N1 = 1; OTHERWISE; N1 = 2; SWITCH N1,(P1,P2,P3); P1.. A(I2+1,2) = -X2.W(1,I) .400.0/U(1); A(I2+1,3) = -A(I2+1,2); GO TO P4; P2.. A(I1+I2,1) = X2.V(I1 - 1,I)/X1.X1. U(I1).RAD(I1); A(I1+I2,3) = X2.V(I1,I)/X1.X1.U(I1).RAD(I1); A(I1+I2,2) = -A(I1+I2,1) - A(I1+I2,3) ; GO TO P4; P3..A(8+I2,1) = X2. 160.0.V(7,I)/U(8).RAD(8); A(8+I2,3) = X2.640.0.V(8,I)/U(8).RAD(8); A(8+I2,2) = - A(8+I2,1) - A(8+I2,3); P4.. END END;

```
COMMENT FORMATION OF CONSTANT VECTORS USED IN GAUSSIAN ELIMINATION;
FOR I = (1,1,38); BEGIN W(I,2) = 1.0 - K.A(I,2) + K.A(I,1).W(I,1);
W(I+1,1) = - K.A(I,3)/W(I,2) END; W(20,1) = 0.0; W(39,1) = 0.0; IF S(3);
WRITE(;;ANS2,FORM2); IF S(4); GO TO TRANS; GO TO BOSS3; OUTPUT ANS2(FOR
I1 = (1,1,38);(FOR I2 = 1,2,3 ; A(I1,I2),FOR I2 = 1,2;W(I1,I2)),W(39,1))
END TWO;

SEGMENT THREE; BEGIN COMMENT SEGMENT 3A; COMMENT SEGMENT 3 IS THE
WORKING PROGRAM THAT GIVES THE SOLUTION TO THE APPROXIMATE BOUNDARY VALUE
PROBLEM.; COMMENT SEGMENT 3A USES A BACKWARD DIFFERENCE APPROXIMATION TO
THE Z-DERIVATIVE, AND OBTAINS A SOLUTION TO THE RESULTING SYSTEM OF NON-
LINEAR EQUATIONS BY ITERATION; ORIG3.. READ(;;DATA3); READ(;; DATA6);
B(12) = B(9)*(B(10) + B(11)); B(2) = B(24)/B(19).B(9); B(5) = B(31).
B(24)/(B(19)- B(7)); WRITE(;;DATA7,LIST7); WRITE(;;DATA4,LIST4); FOR J =
(1,1,19); V(J+19,1) = (V(J+19,1) + 273.2)/B(7); FOR J = (1,1,10);
DELTJ(J)= DELTJ(J)/B(7); VW(3,1) = (VW(3,1) + 273.2)/B(7); VW(1,1) =
V(19,1); VW(2,1) = V(38,1); VW(3,2) = VW(3,1) + DELTJ(1); B(14) =
B(14)/B(7); N1 = N2 = N3 = N4 = 1; ENTER NEWT; WRITE(;;DATA5,LIST5);
FLOAV(1,V(,),U(),RAD();C,T); WRITE(;;ANS4,FORM4); J1(1) = J1(7) =
J1(9) = 1; J1(8) = FIX(Z1(2)/K); J1(10) = FIX(Z2(1)/K);

COMMENT FORMATION OF Z-DERIVATIVE VECTOR; ENTER RVEC; STEP1..
X1 = VW(1,1); FOR I1 = 0,19; BEGIN IF I1 EQL 19; X1 = VW(2,1); V(I1+1,4) =
A(I1+1,2).V(I1+1,1) + A(I1+1,3).V(I1+2,1) - R(I1+1,1)/U(1); FOR I =
(2,1,18); V(I+I1,4) = A(I+I1,1).V(I+I1-1,1)+A(I+I1,2),V(I+I1,1) +
A(I+I1,2).V(I+I1+1,1) - R(I+I1,1)/U(I); V(I1+19,4) = A(I1+19,1).V(I1+
18,1) + A(I1+19,2).V(I1+19,1) + A(I1+19,3).X1 - R(I1+19,1)/U(19) END;
```

```
COMMENT PREDICTOR FORMULA; FOR I = (1,1,38); BEGIN V(I,2) =
V(I,1) + K.V(I,4); V(I,4) = V(I,2) END; N1 = N3 = N4 = 2; N2 = 1;
ENTER NEWT;

COMMENT CORRECTOR FORMULA; ENTER RVEC; J1(2) = 1; STEP2..
FOR I = (1,1,38); W(I+1,3) = (V(I,1) - (K.R(I,2)/U(I)) + K.A(I,1).
W(I,3))/W(I,2); W(20,3) = W(20,3) + K.A(19,3).VW(1,2)/W(19,2); W(39,3) =
W(39,3) + K.A(38,3).VW(2,2)/W(38,2); FOR I = (38,-1,1); V(I,3) =
W(I+1,3) - W(I+1,1).V(I+1,3); N1 = N4 = 3; N2 = N3 = 2; ENTER NEWT;

COMMENT TEST; FOR I = (1,1,19); BEGIN Q = (ABS(V(I,2) - V(I,3))
GTR B(13)) OR (ABS(V(I+19,2)-V(I+19,3)) GTR B(14)); IF Q  BEGIN I = 1;
GO TO STEP3 END END; Q = (ABS(VW(1,2)-VW(1,3)) GTR B(13)) OR (ABS(VW
(2,2) - VW(2,3)) GTR B(14));

COMMENT SHIFT; STEP3.. FOR I = (1,1,38); V(I,2) = V(I,3); N1 = 2;
ENTER RVEC; VW(1,2) = VW(1,3); VW(2,2) = VW(2,3); IF Q; BEGIN J1(2) =
J1(2) + 1; GO TO STEP 2 END; FOR I = (1,1,38); IF V(I,2) LSS 0.0;
BEGIN N1 = 2; GO TO BOSS4 END; IF (VW(1,2)LSS 0.0) OR(VW(2,2) LSS 0.0);
BEGIN N1 = 2; GO TO BOSS4 END; FOR I = (1,1,38); W(I,3) = V(I,4) - V(I,2);
X1 = 0.0; X2 = 0.0; X3 = 0.0; X4 = 0.0; FOR I = (1,1,19); BEGIN X1 = X1 +
W(I,3).W(I,3); IF ABS(W(I,3)) GTR ABS(X2); BEGIN I3 = I; X2 = W(I,3) END;
X3 = X3 + W(I+19,3).W(I+19,3); IF ABS(W(I+19,3)) GTR ABS(X4); BEGIN I4 =
I; X4 = W(I+19,3) END END; FLOAV(2,V(,),U(),RAD();C,T); FLOAV(2,R(,),U(),
RAD();RC,RT);

COMMENT PRINT PROFILES ON DEMAND; IF S(1); WRITE(;;ANS3,FORM3);

COMMENT PRINT PROFILES AS PROGRAMMED; IF S(2); BEGIN IF J1(1)
EQL J1(10); BEGIN WRITE(;;ANS 3,FORM3); WRITE(;;ANS5,FORM5) END; IF J1(1)
```

```
EQL J1(10) + 1; BEGIN WRITE (;;ANS3,FORM3); J1(9) = J1(9) + 1; J1(10) =
FIX(Z2(J1(9))/K) END END;

      COMMENT PRINT AVERAGE CONCENTRATION, TEMPERATURE, RATES, AND ERROR
ESTIMATES. PRINT STEP NUMBER AND NUMBER OF ITERATIONS.; WRITE(;;ANS4,FORM
4);

      COMMENT ADD TO STEP COUNTER AND SHIFT SUBSCRIPTS; J1(1) = J1(1) + 1;
FOR I = (1,1,38); BEGIN V(I,1) = V(I,2); R(I,1) = R(I,2) END; VW(1,1) =
VW(1,2); VW(2,1) = VW(2,2); VW(3,1) = VW(3,2);

      COMMENT GET JACKET TEMPERATURE FOR NEXT STEP; IF J1(1) EQL J1(8);
BEGIN J1(7) = J1(7) + 1; J1(8) = FIX(Z1(J1(7) + 1)/K) END; VW(3,2) =
VW(3,1) + DELTJ(J1(7)); UNTIL J1(1) EQL J1(3); GO TO STEP 1; IF S(3);
GO TO ORIG3; GO TO TRANS; INPUT DATA3(FOR J = (1,1,38);V(J,1), VW(3,1),
FOR J = (1,1,10);(Z1(J),DELTJ(J)),FOR J = (1,1,10); Z2(J),ORD,J1(3));
INPUT DATA6(FOR J = 1,(6,1,11),13,14,15,31;B(J),S(1),S(2),S(3)); OUTPUT
DATA4(FOR J = (1,1,10);(J,Z2(J),Z1(J),DELTJ(J)),ORD,J1(3), VW(3,1),
FOR J = (1,1,19);(RAD(J),V(J,1),V(J+19,1))); OUTPUT DATA7(FOR J =
(1,1,17),31;(J,B(J))); OUTPUT DATA5(VW(1,1).B(9),VW(2,1).B(7)-273.2);
OUTPUT ANS3(FOR L + (1,1,19);(RAD(L),V(L,2).B(9),V(L+19,2).B(7)-273.2,
W(L,3),W(L+19,3),R(L,2)/B(2),R(L+19,2)/B(5)),VW(1,2).B(9), VW(2,2).
B(7)-273.2); OUTPUT ANS4(J1(1), J1(2), C.B(9),T.B(7)-273.2,VW(3,2).B(7) -
273.2, SQRT(X1),X2,I3,SQRT(X3),X4,I4,RC,RT); OUTPUT ANS5(Z2(J1(9)),Z2(J1
(9))/K);

      SEGMENT FOUR; COMMENT SPECIAL OUTPUTS FOR TOUBLES; BEGIN ORIG4..
IF N1 EQL 1; BEGIN WRITE(;;MS1,MFT1); STOP 0000100000; GO TO TRANS END;
IF N1 EQL 2; BEGIN WRITE(;; MS2,MFT2); STOP 0000200000; GO TO TRANS END;
```

```
OUTPUT MS1(J1(1),X2,J1(4),FOR I = 1,2,3;(V(19,I).B(9),VW(1,I),B(9),
V(38,I).B(7)- 273.2,VW(2,I).B(7)-273.2,VW(3,I).B(7)-273.2)); OUTPUT
MS2(J1(1),J1(2),FOR I = (1,1,19);(RAD(I),V(I,2).B(9),V(I+19,2).B(7)-
273.2),VW(1,2).B(9),VW(2,2).B(7)-273.2) END FOUR; FINISH;
```

Nomenclature

In the table of nomenclature that follows, a list of program variables that have the same meanings throughout the program is given first. Then the sets of input and output data are shown in the order of their appearance. The dimensions of all input and output data are in the metric system of units.

Program Variable	Thesis Nomenclature or Explanation
B(1)	B in $k_R' = \exp(B - \frac{E}{R_g T})$
B(2)	$Q_2 = \frac{LU^* \nu}{u \rho c_1^o}$
B(3)	$P_2 = L D^* / \bar{u} r_w^2$
B(4)	$P_1 = L K^* / \bar{u} r_w^2$
B(5)	$Q_1 = \frac{R_g L H_R U^*}{E \bar{u} Z \rho}$
B(6)	$A_x = \frac{h_{Tx} r_w}{k_{Tw}}$
B(7)	E / R_g
B(8)	Δ_s
B(9)	c_1^o
B(10)	m
B(11)	n m and n are constants in the expression $dC/dt = - k_R(T) C^n (C + \delta_3)^m$
B(12)	$(C_1^o)^{m+n} \left(\frac{\nu_2}{\nu_1}\right)^m$

B(13) This is a constant, the maximum permissible change of $c(s_i, z_n) = c_i^o \gamma(s_i, z_n)$ from one iteration to the next. The iterative process for the solution of equation 114 is continued until this condition is satisfied.

B(14) This is a constant, the maximum permissible change of $T(s_i, z_n) = \frac{E\theta}{R_g}(s_i, z_n) - 273.2$ from one iteration to the next. (see B(13)).

B(15) This is a constant, the minimum permissible value of the Jacobian in the Newton's method subroutine. If the value of the Jacobian is less than this, an error message is printed.

B(16) D^* = least upper bound of $D(s_i)$.

B(17) K^* = least upper bound of $K(s_i)$.

B(18) $N_{Re} = \frac{2 r_w \bar{u}}{\nu}$

B(19) $\bar{u}$

B(20) ν

B(21) D_m

B(22) K_m

B(23) r_w

B(24) L

B(25) α_m

B(26) α_H

B(27) ω_a

B(28) ω_b

B(29) f_F

B(30) ω_c

B(31)	H_R / Zp
K	(Δz)
ORD	This is an integer constant that permits the use of special rate expressions for first and second order reaction rates. ORD = 1 is used for first order. ORD = 2 is used for second order. ORD = 3 is used for general rate expression in which B(10) and B(11) must be specified. ORD = 4 is used for no reaction.
J1(1)	This is an integer variable that counts the number of computation steps taken in the z direction.
J1(2)	This is an integer variable that counts the number of iterations for a single computation step in the z direction.
J1(3)	This is an integer constant, the number of the final step to be taken in the z direction.
J1(4)	This is an integer variable that counts the number of iterations performed in the Newton's method subroutine (NEWT).
J1(5) J1(6)	These are integer constants used in Segment One to fix the (Δs) interval for the integration of equation 106c by Simpson's rule.
S(1) through S(4)	These are Boolean constants that control transfer and printing.
RAD(I)	s_i where $I = i + 1$, $i = 0, 1, \ldots, 19$.
U(I), U(I + 9)	$\hat{u}(s_i)$ $i = 0, 1, \ldots, 19$.
DATA 1	See list above.
DATA 2	See list above.

ANS 1

RAD(I), U(I)	See list above.
(1.0 - RAD(I))·X2	$y^+(s_i)$
U(I) / X1	$u^+(s_i)$
B(16),B(17),B(3),B(4)	See list above.
W(I,3)	$\frac{\ell_p}{r_w}(s_i)$, I = i + 1, i ≠ 0
B(16)·W(I,1)	$D(s_i)$, I = i + 1
B(16)·V(I,1)	$D(s_i + \frac{1}{2}\Delta s)$, I = i + 1
B(17)·W(I,2)	$K(s_i)$, I = I + 1
B(17)·V(I,2)	$K(s_i + \frac{1}{2}\Delta s)$, I = i + 1

ANS 2

A(I1, I2)	These are the non-zero constants in $\left(\frac{\vec{P}}{u}\right)\cdot[A]$.
W(I1, I2)	These are constants derived from $\left(\frac{\vec{P}}{u}\right)\cdot[A]$. and used in the Gaussian elimination solution of equation 114.

DATA 3

V(J, 1)	$\vec{V}(s_i, 0)$, J = i + 1. The elements of this vector are the initial values of $T(s_i)$, °C, and $\gamma(s_i)$, dimensionless.
VW(3, 1)	$T_J(0)$. This is the initial value of the jacket temperature, °C.
DELTJ(J)	These are the J^{th} increments of T_J per step of computation in the z direction.
Z1(J)	These are the corresponding values of z where the use of the J^{th} increment of T_J is to begin.
ORD	See list above.

Z2(J)	These are the values of z where profiles of $C(s_i, z)$ and $T(s_i, z)$ are to be printed.
DATA 6	See list above.
DATA 4	See list above and DATA 3.
DATA 7	See list above.
DATA 5	
VW(1,1)·B(9)	$C_w(0)$. This is the initial concentration at the tube wall.
VW(2,1)·B(7) - 273.2	$T_w(0)$. This is the initial temperature at the tube wall.
ANS 3	
V(L, 2)·B(9)	$C(s_i, z_{n+1})$, L = i + 1
V(L+19)·B(7) - 273.2	$T(s_i, z_{n+1})$, L = i + 1
W(L,3), W(L+19, 3)	These are error indicators.
R(L, 2) / B(2), R(L+19, 2) / B(5)	These are values of relative reaction rate.
VW(1,2)·B(9)	$C_w(z_{n+1})$
VW(2, 2)·B(7) - 273.2	$T_w(z_{n+1})$
ANS 4	
J1(1), J1(2)	See list above.
C·B(9)	This is the value of the average concentration, in the sense of equation 117, computed by the subroutine, FLOAV.
T·B(7) - 273.2	This is the value of the average temperature, in the sense of equation 117, computed by the subroutine, FLOAV.
VW(3.2)·B(7) - 273.2	$T_J(z_{n+1})$

SQRT(X1),X2,I3 SQRT(X3),X4,I4	These numbers concern the maximum and average values of the error indicators, W(,), in ANS 3.
RC, RT	These are average rates computed by the subroutine, FLOAV.

ANS 5

Z2(J1(9))	This is the value of z where profiles of C and T are to be printed.
Z2(J1(9))/K	This is the step number corresponding to the above value of z.

MS1

X2	This is the value of the Jacobian in the Newton's method subroutine, NEWT. The other elements of this data set are described in ANS 3 and ANS 4.
MS2	See ANS 3.

APPENDIX III

ISOTHERMAL VELOCITY DATA

Test V1

N_{Re} = 4800, $\bar{u}/u_{max}$ = 0.753

f_F = 0.00985, $\bar{u}$ = 20.7 cm./sec.

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
0.014	5.4	2.3	3.7
0.035	7.4	5.9	5.1
0.066	13.0	11.1	8.9
0.087	15.3	14.6	10.5
0.108	16.5	18.1	11.4
0.129	18.2	21.6	12.6
0.149	19.4	24.9	13.4
0.170	20.1	28.5	13.9
0.207	21.5	34.6	14.8
0.263	22.3	42.4	15.4
0.315	23.1	52.8	15.9
0.417	24.2	69.8	16.7
0.520	25.2	87.0	17.4
0.622	25.8	104	17.8
0.724	26.2	121	18.1
0.827	26.8	138	18.5
0.929	27.2	156	18.8
1.000	27.5	168.4	19.0
0.724	26.5	121	18.3
0.417	24.1	69.8	16.6

Test V2

N_{Re} = 5040

f_F = 0.00970

$\bar{u}$ = 20.75 cm./sec.

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
.014	5.9	2.4	4.1
.066	14.5	11.6	10.0
.118	19.1	20.7	13.2
.170	21.2	29.8	14.7
.222	22.1	38.9	15.3
.376	24.1	65.9	16.7
.581	25.8	102	17.8
.786	26.9	138	18.6
.990	27.2	173	18.8
.960	27.2	168	18.8

Test V3

N_{Re} = 4880

f_F = 0.00975

$\bar{u}$ = 20.65 cm./sec.

$\bar{u}/u_{max}$ = .764

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
.014	5.0	2.3	3.5
.035	7.7	5.9	5.3
.056	12.0	9.5	8.3
.077	14.6	13.1	10.2
.108	17.3	18.4	12.0
.160	19.7	27.3	13.6
.212	21.0	36.2	14.5
.263	21.4	44.8	14.8
.366	23.3	62.6	16.1
.620	25.4	106	17.6
.825	26.5	141	18.3
1.000	27.0	170.5	18.7
.549	24.6	93.6	17.1

Test V4

N_{Re} = 10,150

f_F = 0.00812

$\bar{u}$ = 43.0 cm./sec.

$\bar{u}/u_{max}$ = .788

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
.014	16.2	4.4	5.9
.035	26.3	11.2	9.6
.056	32.6	18.0	11.9
.077	35.8	24.9	13.1
.108	38.4	35.0	14.0
.160	41.1	51.9	15.0
.212	42.7	68.6	15.6
.263	44.1	85.2	16.1
.314	45.6	102	16.6
.314	45.6	102	16.6
.416	47.7	135	17.4
.518	49.7	168	18.1
.622	51.3	202	18.7
.724	52.8	234	19.3
.825	53.4	267	19.5
.927	54.4	300	19.8
1.000	54.6	324	19.9
.724	53.0	234	19.2
.416	48.0	135	17.5

Test V5

N_{Re} = 10,420

f_F = 0.00810

$\bar{u}$ = 43.0 cm./sec.

$\bar{u}/u_{max}$ = .780

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
.014	14.5	4.5	5.3
.035	24.9	11.5	9.1
.056	31.4	18.5	11.5
.077	35.5	25.4	13.0
.108	38.6	35.9	14.1
.139	40.3	46.2	14.7
.160	41.4	53.1	15.1
.222	43.4	73.6	15.8
.222	43.4	73.6	15.8
.273	44.9	90.7	16.4
.376	47.1	125	17.2
.582	51.2	193	18.7
.776	54.1	258	19.7
1.000	55.1	332	20.1
.582	51.4	193	18.7
.273	45.1	90.7	16.5

Test V6

N_{Re} = 10,510

f_F = 0.00805

$\bar{u}$ = 47.2 cm./sec.

$\bar{u}/u_{max}$ = .782

y/r_w (Virtual)	u, cm./sec.	y^+	u^+
.014	17.0	4.6	5.7
.035	29.7	11.5	9.9
.056	35.6	18.5	11.9
.077	39.4	25.5	13.2
.108	42.8	36.0	14.3
.160	45.1	53.2	15.1
.212	47.2	70.5	15.7
.263	48.4	87.5	16.2
.314	50.7	105	17.0
.416	52.5	138	17.6
.622	56.3	207	18.8
.825	58.5	274	19.6
1.000	60.4	333	20.2
.540	54.5	180	18.3
.314	50.9	105	17.0

BIBLIOGRAPHY

1. Damkoehler, G., "Einfluss von Diffusion, Stromung, and Warmetransport auf die Ausbeute bei chemisch-technischen Reaktionen," Der Chemie-Ingenieur, ed. A. Euken and M. Jacob, Part 1, Vol. 3, pp. 359-485, Akademische Verlagsgesellschaft M. B. H., Leipzig (1939).

2. Vlugter, J. C. (Chairman), Syllabus of the 12th Meeting of the European Federation of Chemical Engineering, Amsterdam, May, 1957 Published in Chemical Engineering Science 8, p. 1 (1958).

3. Hougen, O. A. and K. M. Watson, Chemical Process Principles, p. 860, John Wiley and Sons, Inc., New York (1947).

4. Denbigh, K. G., "Velocity and Yield in Continuous Reaction Systems," Transactions of the Faraday Society 40, 352-372 (1944).

5. Walas, S. M., Reaction Kinetics for Chemical Engineers, McGraw-Hill Book Company, Inc., New York (1959).

6. Broetz, W., Grundriss der chemischen Reaktionstechnik, Verlag Chemie G. m. b. H., Weinheim (1958).

7. Bosworth, R. C. L., Transport Processes in Applied Chemistry, Horowitz Publications Inc., Sydney (1956).

8. Prager, S., "Transport Processes with Chemical Reactions," Chemical Engineering Progress Symposium Series 55, No. 25 ("Reaction Kinetics and Unit Operations"), 11-22 (1959).

9. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley and Sons, Inc., New York (1960).

10. Sherwood, T. K., "Mass, Heat, and Momentum Transfer between Phases," Chemical Engineering Progress Symposium Series 55, No. 25 ("Reaction Kinetics and Unit Operations"), 71-85 (1959).

11. Knudsen, J. G. and D. L. Katz, Fluid Dynamics and Heat Transfer, McGraw-Hill Book Company, Inc., New York (1958).

12. Hinze, J. O., Turbulence, McGraw-Hill Book Company, Inc., New York (1958).

13. Sleicher, C. A., Jr., Heat Transfer in a Pipe with Turbulent Flow and Arbitrary Wall-Temperature Distribution, Ph. D. Thesis, University of Michigan (1956). Also see Sleicher, C. A., Jr., "Experimental Velocity and Temperature Profiles for Air in Turbulent Pipe Flow," Transactions of the American Society of Mechanical Engineers 80, 693-704 (1958)

14. Laufer, J., "The Structure of Turbulence in Fully Developed Pipe Flow," National Advisory Committee for Aeronautics, Report 1174 (1958).

15. Reichardt, H., "The Principles of Turbulent Heat Transfer," Trans. S. Reiss, National Advisory Committee for Aeronautics, Technical Memorandum 1408, p. 40 (1957).

16. Rothfus, R. R., D. H. Archer, and K. G. Sikchi, "Distribution of Eddy Viscosity and Mixing Length in Smooth Tubes," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 4, 27-32 (1958).

17. Knudsen and Katz, Ref. 11, pp. 212-222.

18. Laufer, Ref. 14, p. 6.

19. Macmillan, F. A., "Experiments on Pitot Tubes in Shear Flow," Aeronautical Research Council Reports and Memoranda, Reports and Memoranda No. 3028 (1957).

20. Stanton, T. E., "The Mechanical Viscosity of Fluids," Proceedings of the Royal Society of London, Series A, 85, 366-376 (1911).

21. Stanton, T. E. and J. R. Pannell, "Similarity of Motion in Relation to the Surface Friction of Fluids," Philosophical Transactions of the Royal Society of London, Series A, 214, 199-224 (1914).

22. Nikuradse, J., "Gesetzmässigkeiten der Turbulenten Strömung in Glatten Rohren," Vereines Deutscher Ingenieure Forschungsheft, No. 356 (1932).

23. Fage, A., "Turbulent Flow in a Circular Pipe," The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 7th Series, 21, 80-105 (1936).

24. Reichardt, H., "Heat Transfer through Turbulent Friction Layers," Trans. L. M. K. Boelter, National Advisory Committee for Aeronautics, Technical Memorandum 1047 (1940).

25. Deissler, R. G., "Analytical and Experimental Investigation of Adiabatic Turbulent Flow in Smooth Tubes," National Advisory Committee for Aeronautics, Technical Note 2138 (1950).

26. Rothfus, R. R., C. C. Monrad, and V. E. Senecal, "Velocity Distribution and Fluid Friction in Smooth Concentric Annuli," Industrial and Engineering Chemistry 42, 2511-2520 (1950).

27. Senecal, V. E. and R. R. Rothfus, "Transition Flow of Fluids in Smooth Tubes," Chemical Engineering Progress 49, 533-538 (1953).

28. Nunner, W., "Wärmeübergang und Druckabfall in rauhen Rohren," Vereines Deutscher Ingenieure Forschungsheft, No. 455 (1956).

29. Weissberg, H. L., Velocity and Pressure Distributions in Turbulent Pipe Flow with Uniform Wall Suction, Ph. D. Thesis, University of Tennessee, Knoxville, Tennessee (1955). Also see H. L. Weissberg and A. S. Berman, "Velocity and Pressure Distributions in Turbulent Pipe Flow with Uniform Wall Suction," 1955 Heat Transfer and Fluid Mechanics Institute, Reprints of Papers, Paper XIV, University of California, Los Angeles (June, 1955).

30. Isakoff, S. E. and T. B. Drew, "Heat and Momentum Transfer in Turbulent Flow of Mercury," Proceedings of the General Discussion on Heat Transfer of the Institute of Mechanical Engineers and The American Society of Mechanical Engineers, pp. 405-409, London (September, 1951).

31. Rothfus, R. R. and C. C. Monrad, "Correlation of Turbulent Velocities for Tubes and Parallel Plates," Industrial and Engineering Chemistry 47, 1144-1149 (1955).

32. Robertson, J. M., "Turbulent Velocity Distribution in Rough Pipe," Proceedings of the Fifth Midwestern Conference on Fluid Mechanics, pp. 67-84, University of Michigan, Ann Arbor, Michigan (April, 1957).

33. Sherwood, T. K. and B. B. Woertz, "The Role of Eddy Diffusion in Mass Transfer between Phases," Transactions of the American Institute of Chemical Engineers 35, 517-540 (1939).

34. Page, F., Jr., W. G. Schlinger, D. K. Breaux, and B. H. Sage, "Point Values of Eddy Conductivity and Viscosity in Uniform Flow Between Parallel Plates," Industrial and Engineering Chemistry 44, 424-430 (1952).

35. Dhanak, A. M., "Momentum and Mass Transfer by Eddy Diffusion in a Wetted-wall Channel," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 4, 190-196 (1958).

36. Abbrecht, P. H. and S. W. Churchill, "The Thermal Entrance Region in Fully Developed Turbulent Flow," ibid. 6, 268-273 (1960).

37. Baldwin, L. V. and T. J. Walsh, "Turbulent Diffusion in the Core of Fully Developed Pipe Flow," ibid. 7, 53-60 (1961).

38. Flint, D. L., H. Kada, and T. J. Hanratty, "Point Source Turbulent Diffusion in a Pipe," ibid. 6, 325-331 (1960).

39. Prandtl. L., "Über die ausgebildete Turbulenz," Proceedings of the 2nd International Congress for Applied Mechanics, Zurich, pp. 62-74 (September, 1926).

40. Lynn, S. and R. R. Rothfus, "Center-line Value of the Eddy Viscosity," A. I. Ch. E. Journal (American Institute of Chemical Engineers), 5, 566 (1959).

41. Brooks, F. A. and S. P. Berggren, "Remarks on Turbulent Transfer Across Planes of Zero Momentum Exchange," Transactions of the American Geophysical Union 25, part 6, pp. 889-894 (1944).

42. von Kármán, T., "The Analogy between Fluid Friction and Heat Transfer," Transactions of the American Society of Mechanical Engineers 61, 705-710 (1939).

43. Ross, D., "A New Analysis of Nikuradse's Experiments on Turbulent Flow in Smooth Pipes," Proceedings of the Third Midwestern Conference on Fluid Mechanics, pp. 651-667, University of Minnesota, Minneapolis, Minnesota (March, 1953).

44. Deissler, R. G., "Analysis of Turbulent Heat Transfer, Mass Transfer, and Friction in Smooth Tubes at High Prandtl and Schmidt Numbers," National Advisory Committee for Aeronautics, Report 1210 (1955).

45. Ruth, B. F. and H. H. Yang, "An Empirical Correlation for Velocity Distribution of Turbulent Fluid Flow," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 3, 117-120 (1957)

46. Rannie, W. D., "Heat Transfer in Turbulent Shear Flow," Journal of the Aeronautical Sciences 23, 485-489 (1956).

47. Van Driest, E. R., "On Turbulent Flow Near a Wall," 1955 Heat Transfer and Fluid Mechanics Institute, Reprints of Papers, Paper XII, University of California, Los Angeles (June, 1955).

48. Franklet, D. L., Heat Transfer to Liquid Metals Flowing Turbulently in a Pipe, Ph. D. Thesis, Georgia Institute of Technology, Atlanta Georgia (1958).

49. Gill, W. N. and M. Scher, "A Modification of the Momentum Transport Hypothesis," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 7, 61-63 (1961).

50. Hefner, R. J., Momentum and Heat Transfer to a Fluid Flowing Turbulently in a Pipe, Ph. D. Thesis, Georgia Institute of Technology, Atlanta, Georgia (1959).

51. Corcoran, W. H., J. B. Opfell, and B. H. Sage, Momentum Transfer in Fluids, pp. 199-204, Academic Press, Inc., New York (1956).

52. Tien, C. L., "On the Eddy Diffusivities for Momentum and Heat," Applied Scientific Research A8, 345-348 (1958/1959).

53. Bosworth, R. C. L., "Distribution of Reaction Times for Laminar Flow in Cylindrical Reactors," The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, Series 7, 39, 847-862 (1948).

54. Bosworth, R. C. L., "Distribution of Reaction Times for Turbulent Flow in Cylindrical Reactors," The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, Series 7, 40, 314-324 (1949).

55. Danckwerts, P. V., "Continuous Flow Systems, Distribution of Residence Times," Chemical Engineering Science 2, 1-13 (1953).

56. Taylor, G. I., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube," Proceedings of the Royal Society of London, Series A, 219, 186-203 (1953).

57. Taylor, G. I., "The Dispersion of Matter in Turbulent Flow Through a Pipe," ibid., 223, 446-486 (1954).

58. Tichacek, L. J., C. H. Barkelew, and T. Baron, "Axial Mixing in Pipes," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 3, 439-442 (1957).

59. Kramers, H. and G. Alberda, "Frequency Response Analysis of Continuous Flow Systems," Chemical Engineering Science 2, 173-181 (1953).

60. Friend, W. L. and A. B. Metzner, "Turbulent Heat Transfer Inside Tubes and the Analogy Among Heat, Mass and Momentum Transfer," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 4, 393-402 (1958).

61. Reichardt, Ref. 15, pp. 14-21.

62. Jenkins, R., "Variation of the Eddy Conductivity with Prandtl Modulus and its Use in Prediction of Turbulent Heat Transfer Coefficients," 1951 Heat Transfer and Fluid Mechanics Institute, Preprints of Papers, pp. 147-158, Stanford University, Palo Alto, California (June, 1951).

63. Rohsenow, W. M. and L. S. Cohen, Massachusetts Institute of Technology Heat Transfer Laboratory, Report (June, 1960). Quoted in W. M. Rohsenow and H. Y. Choi, Heat Mass and Momentum Transfer Prentice-Hall Inc., Englewood Cliffs, New Jersey (1961).

64. Lykoudis, P. S. and Y. S. Touloukian, "Heat Transfer in Liquid Metals," Transactions of the American Society of Mechanical Engineers 80, 653-666 (1958).

65. Page, F., Jr., W. H. Corcoran, W. G. Schlinger, and B. H. Sage, "Temperature and Velocity Distributions in Uniform Flow Between Parallel Plates," Industrial and Engineering Chemistry 44, 419-424 (1952).

66. Siegel, R. and E. M. Sparrow, "Turbulent Flow in a Circular Tube with Arbitrary Internal Heat Sources and Wall Heat Transfer," Transactions of the American Society of Mechanical Engineers 81C, (Journal of Heat Transfer), 280-290 (1959).

67. Schwarz, W. H. and H. E. Hoelscher, "Mass Transfer in a Wetted-wall Column: Turbulent Flow," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 2, 101-106 (1956).

68. Hinze, Ref. 12, p. 525.

69. Hawthorn, R. D., "Effect of Radial Temperature Variation on Axial Mixing in Pipes," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 6, 443-445 (1960).

70. Beek, J., Jr., and R. S. Miller, "Turbulent Transport in Chemical Reactors," Chemical Engineering Progress Symposium Series 55, No. 25 ("Reaction Kinetics and Unit Operations"), 23-29 (1959).

71. Irving, J. P. and J. M. Smith, "Heat Transfer in a Chemically Reacting System (Nitrogen Tetroxide - Dioxide), A. I. Ch. E. Journal (American Institute of Chemical Engineers) 7, 91-96 (1961).

72. Hulburt, H. M., "Chemical Processes in Continuous Flow Systems: Reaction Kinetics," Industrial and Engineering Chemistry 36, 1012-1017 (1944).

73. Wehner, J. F. and R. H. Wilhelm, "Boundary Conditions of Flow Reactors," Chemical Engineering Science 6, 89-93 (1956).

74. D'yakonov, G. K., Voprosi Teorii Podobiya v Oblasti Fiziko-Khimicheskikh Protsessov, Academy of Science of the U. S. S. R., Moscow (1956).

75. Johnstone, R. E. and M. W. Thring, Pilot Plants, Models, and Scale-up Methods in Chemical Engineering, McGraw-Hill Book Company, Inc., New York (1957).

76. Fan, L. and R. C. Bailie, "Axial Diffusion in Isothermal Tubular Flow Reactors," Chemical Engineering Science 13, 63-68 (1960).

77. Eldridge, J. W. and E. L. Piret, "Continuous Flow Stirred-Tank Reactor Systems, 1. Design Equations for Homogeneous Liquid Phase Reactions. Experimental Data," Chemical Engineering Progress 46, 290-299 (1950).

78. Schoenemann, K., "Der chemische Umsatz bei kontinuierlich durchgeführten Reaktionen," Dechema Monographien 21, 203-327 (1952).

79. MacMullin, R. B. and M. Weber, Jr., "The Theory of Short-Circuiting in Continuous-Flow Mixing Vessels in Series and the Kinetics of Chemical Reactions in Such Systems," Transactions of the American Institute of Chemical Engineers 31, 409-458 (1935).

80. Horn, F. and L. Kuechler, "Probleme bei reaktionstechnischen Berechnungen," Chemie - Ingenieur - Technik 31, 1-11 (1959).

81. Broetz, Ref. 6, pp. 300-379.

82. Hougen and Watson, Ref. 3, pp. 874-883.

83. Smith, J. M., Chemical Engineering Kinetics, pp. 130-185, McGraw-Hill Book Company, Inc., New York (1956).

84. Walas, Ref. 5, pp. 101-125.

85. Murdoch, P. G. and C. D. Holland, "Designing Fired Tubular Reactors," Petroleum Refiner 33, No. 3, 159-163, and No. 6, 163-166 (1954).

86. Perkins, T. K. and H. F. Rase, "A Simplified Method for Designing Light Hydrocarbon Cracking Units," Chemical Engineering Progress 52, No. 3, 105M-110M (1956).

87. Bashforth, F. and J. C. Adams, Theories of Capillary Action, Cambridge University Press, Cambridge (1883). Quoted in W. E. Milne, Numerical Solution of Differential Equations, John Wiley and Sons, Inc., New York (1953).

88. Billingsley, D. S., W. S. McLaughlin, Jr., N. E. Welch, and C. D. Holland, "Use of Computers in Reactor Design," Industrial and Engineering Chemistry 50, 741-752 (1958).

89. Bilous, O. and N. R. Amundson, "Chemical Reactor Stability and Sensitivity II. Effects of Parameters on Sensitivity of Empty Tubular Reactors," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 2, 117-126 (1956).

90. Gee, R. E., W. H. Linton, Jr., R. E. Maier, and J. W. Raines, "Use of Computers in Kinetic Calculations. Gas-Phase Tubular Reactor Kinetics Involving Differential Fouling of Heat Transfer Surface," Chemical Engineering Progress 50, 497-502 (1954).

91. Danckwerts, P. V., "The Effect of Incomplete Mixing on Homogeneous Reactions," Chemical Engineering Science 8, 93-102 (1958).

92. Denbigh, K. G., "The Kinetics of Continuous Reaction Processes: Application to Polymerization," Journal of Applied Chemistry 1, 227-236 (1951).

93. Roughton, F. J. W. and G. A. Millikan, "Photoelectric Methods of Measuring the Velocity of Rapid Reactions," Proceedings of the Royal Society of London, Series A, 155, 258-292 (1936).

94. Dalziel, H., "An Apparatus for the Spectrokinetic Study of Rapid Reactions," Biochemical Journal 55, 79-93 (1953).

95. van Heerden, C., "The Character of the Stationary State of Exothermic Processes," Chemical Engineering Science 8, 133-145 (1958).

96. Levenspiel, O. and K. B. Bischoff, "Backmixing in the Design of Chemical Reactors," Industrial and Engineering Chemistry 51, 1431-1433 (1959).

97. Tichacek, L. J., "Selectivity in Experimental Reactors," Paper presented at the 42nd National Meeting, American Institute of Chemical Engineers, Atlanta, Georgia (February, 1960).

98. Cleland, F. A. and R. H. Wilhelm, "Diffusion and Reaction in a Viscous-flow Tubular Reactor," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 2, 489-499 (1956).

99. Crank, J. and P. Nicolson, "A Practical Method for Numerical Evaluation of Solutions of Partial Differential Equations of the Heat-Conduction Type," Proceedings of the Cambridge Philosophical Society 43, 50-67 (1947).

100. Chambré, P., "On the Chemical Reactions in Internal Flow Systems," Applied Scientific Research A9, 157-168 (1959/1960).

101. Jacob, M., Heat Transfer, Vol. 1, John Wiley and Sons, Inc., New York (1949).

102. Sparrow, E. M. and R. Siegel, "Laminar Tube Flow with Arbitrary Internal Heat Sources with Wall Heat Transfer," Nuclear Science and Engineering 4, 239-254 (1958).

103. van Heerden, C., "Autothermic Processes, Properties and Reactor Design," Industrial and Engineering Chemistry 45, 1242-1247 (1953).

104. Broetz, W., Ref. 6, pp. 354-364.

105. Coste, J., R. Aris, and N. R. Amundson, "Tubular Reactor Sensitivity," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 7, 124-128 (1961).

106. Foss, A. S., "Chemical Reaction-System Dynamics," Chemical Engineering Progress Symposium Series 55, No. 25 ("Reaction Kinetics and Unit Operations"), 47-60 (1959).

107. Temkin, M. and V. Pyzhev, "Kinetics of the Synthesis of Ammonia on Promoted Iron Catalysts," Zhurnal Fizicheskoi Khimii 13, 851-867 (1939).

108. Denbigh, K. G., "Optimum Temperature Sequences in Reactors," Chemical Engineering Science 8, 125-132 (1958).

109. Bilous, O. and N. R. Amundson, "Optimum Temperature Gradients in Tubular Reactors I. General Theory and Methods," Chemical Engineering Science 5, 81-92 (1956).

110. Bilous, O. and N. R. Amundson, "Optimum Temperature Gradients in Tubular Reactors II. Numerical Study," ibid. 115-126.

111. Aris, R., "Studies in Optimization - II," Chemical Engineering Science 13, 18-29 (1961).

112. Aris, R., "Studies in Optimization - IV," ibid. 197-206.

113. Horn, F. and U. Troltenier, "Über den optimalen Temperaturverlauf in Reaktionsrohr," Chemie - Ingenieur - Technik 32, 382-393 (1960).

114. Horn, F., "Optimale Temperatur- und Konzentrationsverläufe," Chemical Engineering Science 14, 77-87 (1961).

115. Horn, F., "Über das problem der optimalen Rührkesselkaskade für chemische reaktionen," ibid. 15, 176-187 (1961).

116. van de Vusse, J. G. and H. Voetter, "Optimum Pressure and Concentration Gradients in Tubular Reactors," ibid. 15, 176-187 (1961).

117. Bosworth, Ref. 7, pp. 307-313.

118. Bird, Stewart, and Lightfoot, Ref. 9, pp. 554-572.

119. Prager, Ref. 8, pp. 11-13.

120. Benson, S. W., The Foundations of Chemical Kinetics, p. 67, McGraw-Hill Book Company, Inc., New York (1960).

121. Barkelew, C. H., "Stability of Chemical Reactors," Chemical Engineering Progress Symposium Series 55, No. 25 (Reaction Kinetics and Unit Operations"), 37-46 (1959).

122. Richtmyer, R. D., Difference Methods for Initial-Value Problems, Interscience Publishers, Inc., New York (1957).

123. Collatz, L., The Numerical Treatment of Differential Equations, 3rd ed., Trans. P. G. Williams, Springer Verlag, Berlin (1960).

124. Forsythe, G. E. and W. R. Wasow, Finite-Difference Methods for Partial Differential Equations, John Wiley and Sons, Inc. (1960).

125. Varga, R. S., "On Higher Order Stable Implicit Methods for Solving Partial Differential Equations," Case Institute of Technology Computing Center, Report No. 1029 (1960).

126. Douglas, J., Jr., "On the Relation Between Stability and Convergence in the Numerical Solution of Linear Parabolic and Hyperbolic Differential Equations," Journal for the Society of Industrial and Applied Mathematics 4, 20-37 (1956).

127. Douglas, J., Jr., "On the Numerical Integration of Quasi-linear Partial Differential Equations," Pacific Journal of Mathematics 6 35-42 (1956).

128. Rose, M. E., "On the Integration of Non-linear Parabolic Equations by Implicit Difference Methods," Quarterly of Applied Mathematics 14, 237-248 (1956).

129. Lees, M., "Approximate Solutions of Parabolic Equations," Journal for the Society of Industrial and Applied Mathematics 7, 167-183 (1959).

130. Bird, Stewart, and Lightfoot, Ref. 9, pp. 554-571.

131. Prigogine, I. and R. Defay, Chemical Thermodynamics, Trans. D. H. Everett, p. 11, Longmans, Green and Co., London (1954).

132. ibid., p. 468.

133. Birkhoff, Garret, Hydrodynamics, 1st ed., pp. 77-115, Dover Publications, Inc., New York (1955).

134. Towle, W. L. and T. K. Sherwood, "Eddy Diffusion - Mass Transfer in the Central Portion of a Turbulent Air Stream," Industrial and Engineering Chemistry 31, 457-462 (1939).

135. Brown, H. E., B. H. Amstead, and B. E. Short, "Temperature and Velocity Distribution and Transfer of Heat in a Liquid Metal," Transactions of the American Society of Mechanical Engineers 80, 693-704 (1958).

136. Hinze, Ref. 12, pp. 420-428.

137. ibid., p. 426.

138. ibid., p. 428.

139. Toor, H. L., "Turbulent Diffusion and the Multicomponent Reynolds Analogy," A. I. Ch. E. Journal (American Institute of Chemical Engineers) 6, 525-527 (1960).

140. Prigogine and Defay, Ref. 131, p. 13.

141. Hartree, D. R. and J. R. Womersley, "A Method for the Numerical or Mechanical Solution of Certain Types of Partial Differential Equations," Proceedings of the Royal Society of London, Series A, 161, 353-366 (1937).

142. Varga, R. S., Iterative Numerical Analysis, pp. 6.1-6.5 and 10.1-10.19, Computation and Data Processing Center, University of Pittsburgh (1959).

143. Frazer, R. A., W. J. Duncan, and A. R. Collar, Elementary Matrices and Some Applications to Dynamics and Differential Equations, pp. 156-243, Cambridge University Press, Cambridge (1938).

144. Hamming, R. W., "Stable Predictor-Corrector Methods for Ordinary Differential Equations," Journal of the Association for Computing Machinery 6, 37-47 (1959).

145. Forsythe and Wasow, Ref. 124, p. 103.

146. Richtmyer, Ref. 122, pp. 98-101.

147. Ower, E., The Measurement of Air Flow, 3rd. ed. rev., pp. 209-239, Chapman and Hall Ltd., London (1949).

148. Prandtl, L. and O. G. Tietjens, Applied Hydro- and Aeromechanics, Trans. J. P. Den Hartog, pp. 226-240, McGraw-Hill Book Company, Inc., New York (1934).

149. Chattock, A. P., W. E. Walker, and E. H. Dixon, "On the Specific Velocities of Ions in the Discharge from Points," The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 6th Series, 1, 79-98 (1901).

150. Douglas, G. P., "Note on a Large Range Manometer for Wind Channel Work," Technical Report of the Advisory Committee for Aeronautics, Reports and Memoranda No. 657, pp. 110-111, Vol. 1 (1919-1920).

151. Thon, N., ed., Tables of Chemical Kinetics Homogeneous Reactions, (Circular 510) National Bureau of Standards, Washington (1951).

152. Young, A. D. and J. N. Maas, "The Behaviour of a Pitot Tube in a Transverse Total Pressure Gradient," Aeronautical Research Committee Reports and Memoranda, Reports and Memoranda No. 1770 (1937).

153. Macmillan, F. A., "Viscous Effects on Pitot Tubes at Low Speeds," Journal of the Royal Aeronautical Society 58, 570-572 (1954).

154. Deissler, Ref. 25, p. 20.

155. McAdams, W. H., Heat Transmission, 3rd ed., p. 219, McGraw-Hill Book Company, Inc. New York (1950).

156. Perry, J. H., ed., Chemical Engineers Handbook, 3rd ed., p. 456, McGraw-Hill Book Company, Inc., New York (1950).

157. McAlister, J. A. personal communication.

158. Tribus, M. and L. M. K. Boelter, "An Investigation of Aircraft Heaters, II Properties of Gases," National Advisory Committee for Aeronautics, Wartime Report W-9 (October 1942).

159. Reicher, L. T., "Ueber die Geschwindigkeit der Verseifung," Justus Liebig's Annalen der Chemie 228, 257-287 (1885).

160. Skrabal, A. and A. M. Hugetz, "Über den Einfluss der Alkoholkomponente auf die Verseifungsgeschwindigkeit der Essigsäureester," Monatshefte für Chemie und Verwandte Teile anderer Wissenschaften 47, 17-38 (1926).

161. Rylander, P. N. and D. S. Tarbell, "Cleavage of the Carbon-Sulfur Bond. Rates of Hydrolysis of Some Alkyl Acetates and the Corresponding Thiolacetates in Aqueous Acetone," Journal of the American Chemical Society 72, 3021-3025 (1950).

162. Newling, W. B. S. and C. N. Hinshelwood, "The Kinetics of the Acid and Alkaline Hydrolysis of Esters," Journal of the Chemical Society (London) 1936, pp. 1357-1361.

163. Smith, L. and H. Olsson, "Die Abhängigkeit der alkalischen Hydrolyse-geschwindigkeit von der Konstitution des Alkohols. II," Zeitschrift für Physikalische Chemie, Stöchiometrie, und Verwandschaftslehre 118, 99-106 (1925).

164. Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties (Circular 500), National Bureau of Standards, Washington (February, 1952).

165. Reid, R. C. and T. K. Sherwood, The Properties of Gases and Liquids, Their Estimation and Correlation, pp. 109-114, McGraw-Hill Book Company, Inc., New York (1958).

166. Moelwyn Hughes, E. A., Physical Chemistry, 2nd rev. ed., p. 787, Pergamon Press, London (1961).

167. Marshall, A., "The Vapour Pressures of Binary Mixtures," Journal of the Chemical Society (London) 89, 1350-1386 (1906).

168. Reid and Sherwood, Ref. 165, pp. 283-298.

169. Lykoudis, P. S., Discussion of paper, "Experimental Velocity and Temperature Profiles for Air in Turbulent Pipe Flow," by C. A. Sleicher, Jr., Transactions of the American Society of Mechanical Engineers 80, 702 (1958).

170. Miller, J. C. P., "Extremal Approximations - A Summary," On Numerical Approximation, ed. R. Langer, pp. 330-333, University of Wisconsin Press, Madison, Wisconsin (1959).

171. Lanczos, C., Applied Analysis, pp. 321-324, 331, Prentice Hall, Inc., Englewood Cliffs, New Jersey (1956).

172. ibid., pp. 331-358.

173. ibid., p. 324.

174. Whitaker, S. and R. L. Pigford, "Numerical Differentiation of Experimental Data," Industrial and Engineering Chemistry 52, 185-188 (1960).

175. Bennett, C. A. and N. L. Franklin, Statistical Analysis in Chemistry and the Chemical Industry, pp. 216-273, John Wiley and Sons, Inc., New York (1954).

176. Mood, A. M., Introduction to the Theory of Statistics, pp. 406-410, McGraw-Hill Book Company, Inc., New York (1950).

177. Burroughs Corporation, Burroughs Algebraic Compiler, Detroit (January, 1961).

178. Perlis, A. J. and K. Samelson, "Preliminary Report - International Algebraic Language," The Communications of the Association for Computing Machinery 1, No. 12, 8-22 (1958).

VITA

Olin Maynard Fuller, Jr., was born in Atlanta, Georgia on June 17, 1929. He attended primary and secondary schools in DeKalb County, Georgia and completed his secondary education at Georgia Military Academy, College Park, Georgia.

He enrolled at the Georgia Institute of Technology in 1946 under the Cooperative Plan. His Cooperative Plan employer was Union Carbide Chemicals Corporation, South Charleston, West Virginia. In 1952 he was awarded the degree of Bachelor of Chemical Engineering with Highest Honor.

In 1951, he was employed as an engineer by Union Carbide Chemicals Corporation, South Charleston, West Virginia. He joined the staff of the Research Division of West Point Manufacturing Company, Shawmut, Alabama in 1955.

In 1956, he enrolled in the Graduate Division of the Georgia Institute of Technology to begin work in the School of Chemical Engineering on the degree of Doctor of Philosophy.

He is a Registered Professional Engineer, a member of the Society of Sigma Xi, the American Institute of Chemical Engineers, and the American Chemical Society.

In 1958 he was married to the former Nancy Hines Grayson of Charlotte, North Carolina. They have a daughter, Mary Claire.